# UNIVERSITY OF KWAZULU-NATAL

# SYNTHESIS, CHARACTERIZATION AND CATALYTIC/ANTIBACTERIAL ACTIVITY STUDIES OF $\eta^5$-CYCLOPENTADIENYL DICARBONYL RUTHENIUM(II) AMINE COMPLEXES

By

**NYAWADE EUNICE ADHIAMBO**

MSc (Chemistry)

**MARCH 2015**

# SYNTHESIS, CHARACTERIZATION AND CATALYTIC/ANTIBACTERIAL ACTIVITY STUDIES OF $\eta^5$-CYCLOPENTADIENYL DICARBONYL RUTHENIUM(II) AMINE COMPLEXES

**NYAWADE EUNICE ADHIAMBO**

MSc (Chemistry)

A thesis submitted to the School of Chemistry, College of Agriculture, Engineering and Science, University of KwaZulu-Natal, in fulfilment of the academic requirements for the degree of Doctor of Philosophy.

This thesis has been written according to format 4 as stipulated in the guidelines from the College of Agriculture, Engineering and Science. The chapters consist of an overall introduction, discrete research papers and a final discussion. Some of the research papers have been published in internationally recognized, peer-reviewed journals.

As the candidate's supervisor, I have approved this thesis for submission.

**Supervisor:** Prof. Holger B. Friedrich

Signed: ---------- Date: ----------

March 2015

## ABSTRACT

The reaction of $(\eta^5\text{-}C_5H_5)Ru(CO)_2I$ and $AgBF_4$ in the ratio of 1:1 in methylene chloride afforded the iodo-bridged ruthenium complex, $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2I$. Two polymorphs, **I** and **II,** of the complex $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2I$ were isolated. Polymorph **I** crystallized in the monoclinic P2/c space group with a = 12.0982(5) Å, b = 9.7923(4) Å, c = 15.5321(6) Å, β = 102.9880(10)°, while polymorph **II** crystallized in the monoclinic $P2_1/c$ with a = 7.00560(10) Å, b = 14.1446(3) Å, c = 18.2226(3) Å, β = 96.2390(10)°. The reaction of $(\eta^5\text{-}C_5H_5)Ru(CO)_2I$ and a slight excess of $AgBF_4$ in methylene chloride afforded the Lewis acid, $[CpRu(CO)_2]^+BF_4$, which was subsequently reacted with slight excesses of 1-alkanamines, $RNH_2$, in dry dichloromethane affording the new water-soluble 1-alkanaminedicarbonyl($\eta^5$-cyclopentadienyl)ruthenium(II) tetrafluoroborate complexes, $[CpRu(CO)_2NH_2R]^+BF_4^-$ (Cp = $\eta^5\text{-}C_5H_5$; R = $CH_3$, $C_2H_5$, $C_3H_7$, $C_4H_9$**,** $C_5H_{11}$ and $C_6H_{13}$). Complexes of the type, $[CpRu(CO)_2L]^+BF_4^-$, (L = $C_6H_{11}NH_2$, $C_6H_5CH_2NH_2$, $C_6H_5CH(CH_3)NH_2$, $(CH_3)_2CHNH_2$, $CH_2CHCH_2NH_2$, $NH_2CH_2(C_6H_4)OCH_3$, $NH_2CH_2C_6H_4CN$, $NH_2(CH_3)_3C_6H_2$) were also synthesized by the reaction of the Lewis acid, $[CpRu(CO)_2]^+BF_4$, with the ligands, L.

The reaction of $(\eta^5\text{-}C_5(CH_3)_5)Ru(CO)_2I$ and a slight excess of $AgBF_4$ in methylene chloride afforded the Lewis acid, $[Cp^*Ru(CO)_2]^+BF_4$ (Cp* = $\eta^5\text{-}C_5(CH_3)_5$), which was subsequently reacted with slight excesses of 1-alkanamine, $RNH_2$ (R = $CH_3$, $C_2H_5$, $C_3H_7$, $C_4H_9$**,** $C_5H_{11}$), in dry dichloromethane affording the new water-soluble complex salts, $[Cp^*Ru(CO)_2NH_2R]^+BF_4^-$

The α,α′-diaminoalkane-bridged diruthenium complex salts $[Rp_2NH_2(CH_2)_nNH_2]Y_2$ (Rp = $CpRu(CO)_2$, where Cp = $\eta^5\text{-}C_5H_5$; n = 2, 3, 4 and 6; Y = $BF_4$ or $SO_3CF_3$) were synthesized by the reaction of the acetonitrile complexes, $[RpNCCH_3]Y$ and $NH_2(CH_2)_nNH_2$ (n = 2, 3,4 and 6) in the ratio of 2:1.

All the complexes synthesized in this study are new and were fully characterized by IR, NMR, elemental analysis and melting point. The crystal structures of 12 complexes were determined; they all feature a "pseudo-octahedral three-legged piano stool" structure in which the ruthenium centre was coordinated through a sigma bond to the amine N atom and two carbonyl ligands at the base of the stool and the cyclopentadienyl ring as the apex of the stool.

Antimicrobial susceptibility tests were done for the α,α′-diaminoalkane-bridged diruthenium compounds, and some mononuclear complexes, $[CpRu(CO)_2L]^+BF_4^-$. Good antimicrobial activity against Gram-positive and Gram-negative bacteria, as well as mycobacterium, was

achieved. Furthermore, the complexes synthesized showed excellent catalytic activity in the oxidation of styrene to form benzaldehyde in very good yield.

# LIST OF ABBREVIATIONS

| | |
|---|---|
| AMBN | 4-aminomethylbenzonitrile |
| AMP10 | ampicillin |
| ATCC | American tissue culture centre |
| BA | benzylamine |
| bbn | bis[4(4′-methyl-2,2′-bipyridyl)]-1 |
| bda | 2, 2'-bipyridyl-6,6' –dicarboxylate |
| Bipy | 2,2`-bipyridyl |
| Biq | biquinoline |
| Bpy | bipyridine |
| CHA | cyclohexylamine |
| CO | carbon monoxide |
| CO-RMs | CO-releasing molecules |
| Cp | Cyclopentadienyl anion |
| Cp* | Pentamethylcyclopentadienyl anion |
| d | doublet |
| DAB | 1,4-diaminobutane |
| DABCO | 1,4-diazacyclo[2.2.2]octane |
| DAE | 1,2-diaminoethane |
| DAH | 1,6-diaminohexane |
| DAP | 1,3-diaminopropane |
| DEC | N,N-diethyl-4-piperazine-1-carboxamide |
| dmb | 4,4′-dimethyl-2,2′-bipyridine |
| dmp | 2, 9 – dimethylphenanthroline |
| DMSO | dimethyl sulfoxide |
| DNA | Deoxyribonucleic acid |
| DSC | Differential Scanning Calorimetry |
| ESI | electrospray ionization |
| ES-MS | electrospray mass spectrum |
| FTIR | Fourier Transform Infrared |
| $H_2$amp | N-(2-hydroxyphenyl)salicyldimine |
| H2-DAR | dibasic tetradentate diacetyl resorcinol |
| $H_2$pydic | pyridine-2,6-dicarboxylic acid |
| HMTA | hexamethylenetetramine |

| | |
|---|---|
| HRMS | High Resolution Mass Spectroscopy |
| HSQC | heteronuclear single quantum coherence |
| IDSA | Infectious Diseases Society of America |
| IIP | 2-(1H-indol-3-yl)-1H-imidazo[4,5-f][1,10-phenanthroline |
| Im | imidazole |
| iPrA | isopropylamine |
| MBA | α-methylbenzylamine |
| mcpba | m-chloroperbenzoic acid |
| MDR | Multidrug resistant |
| Me | methyl |
| $Me_4$phen | 3,4,7,8-tetramethyl-1,10-phenanthroline |
| MeCN | acetonitrile |
| MeOBA | 4-methoxybenzylamine |
| MH | Mueller-Hinton |
| mmi | 1,3-dimethylimidazolium-2-ylidene |
| MRSA | Methicillin-resistant **S**taphylococcus aureus |
| MTB | Mycobacterium tuberculosis |
| NMO | N-methyl morpholin |
| $^{13}$C NMR | carbon Nuclear Magnetic Resonance |
| $^{1}$H NMR | proton Nuclear Magnetic Resonance |
| ORTEP | Oak Ridge Thermal Ellipsoid Plot |
| PhA | phenylamine |
| Phen | 1,10-phenanthrolin |
| Phen | phenanthroline |
| PhIO | phenyl periodate |
| ppm | parts per million |
| PTA | 1,3,5-triaza-7-phosphatricyclo-[3.3.1.1]decanephosphine |
| s | singlet |
| t | triplet |
| TB | Tuberculosis |
| t-BuOOH | tertbutyl peroxide |
| TE30 | tetracycline |
| TGA | Thermogravimetric analysis |
| THF | Tetrahydrofuran |
| TMA | 2,4,6-trimethylaniline |

| | |
|---|---|
| tmp | 5,10,15,20 – tetramesitylporphyrin |
| tpy | 2,2´:6´,2´´-terpyridine |
| TSA | Tryptone Soya Agar |
| UV | ultraviolet |
| VRE | vancomycin-resistant Enterococcus |
| XDR-TB | extensively drug-resistant TB |

## DECLARATION 1: PLAGIARISM

I, **Nyawade Eunice Adhiambo**, declare that

1. The research reported in this thesis, except where otherwise indicated, is my original research.

2. This thesis has not been submitted for any degree or examination at any other university.

3. This thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.

4. This thesis does not contain other persons' writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted, then:
   a. Their words have been re-written but the general information attributed to them has been referenced
   b. Where their exact words have been used, then their writing has been placed in italics and inside quotation marks, and referenced.

5. This thesis does not contain text, graphics or tables copied and pasted from the Internet, unless specifically acknowledged, and the source being detailed in the thesis and in the References sections.

Signed ……

## DECLARATION 2: PUBLICATIONS

DETAILS OF CONTRIBUTION TO PUBLICATIONS that form part and/or include research presented in this thesis:

**Publications**

1. Nyawade, E. A., Friedrich, H. B., M'thiruaine, C. M. and Omondi, B. Synthesis, characterization and crystal structure of two polymorphs of iodo-bridged ruthenium (1+)tetracarbonylbis($\eta^5$-2,4-cyclopentadien-1-yl) μ-iodidotetrafluoroborate salt. Journal of Molecular Structure 1048 (2013) 426.
   Contributions: I did all the experimental work, characterized the compounds and wrote the paper. Dr. Owaga solved the crystals and proof read the manuscript. Dr. M'thiruaine edited and proof read the manuscript. Prof. Friedrich is my supervisor.

2. Nyawade, E. A., Friedrich, H. B., Omondi, B. Synthesis, characterization and crystal structures of new water-soluble 1-alkanamine-dicarbonyl($\eta^5$-cyclopentadienyl)ruthenium(II) tetrafluoroborate complex salts. Inorganica Chimica Acta 415 (2014) 44
   Contributions: I did all the experimental work, characterized the compounds and wrote the paper. Dr. Owaga solved the crystals and proof read the manuscript. Prof. Friedrich is my supervisor.

3. Nyawade, E. A. and Friedrich, H. B. Synthesis, characterization and structural elucidation of $\eta^5$-pentamethylcyclopentadienyl rutheniuml(II) complex salts of 1-alkanamine. Manuscript
   Contributions: I did all the experimental work, characterized the compounds and wrote the paper. Prof. Friedrich is my supervisor.

4. Nyawade, E. A., Friedrich, H. B., Omondi, B., Chenia, H. Y. Synthesis, characterization and of new α,α′-diaminoalkane-bridged dicarbonyl(η5-

cyclopentadienyl)ruthenium(II) complex salts: Antibacterial activity tests of η5-cyclopentadienyl dicarbonyl ruthenium(II) amine complexes. Submitted

Contributions: I did all the experimental work, characterized the compounds, analysed the antimicrobial test results and wrote the paper. Dr. Owaga solved the crystals and proof read the manuscript. Dr. Chenia prepared the bacteria culture solutions for antimicrobials tests and proof read the manuscript. Prof. Friedrich is my supervisor.

5. Nyawade, E. A., Friedrich, H. B., Mpungose, P. Synthesis and characterization of new η5-cyclopentadienyldicarbonylruthenium(II) amine complexes: Their application as homogeneous catalysts in styrene oxidation. Manuscript

   Contributions: I synthesized and characterized the compounds, analysed the catalysis test data and wrote the paper. Mr. Mpungose did the catalytic tests. Prof. Friedrich is my supervisor.

**CONFERENCE CONTRIBUTIONS**

1. **Poster presentation:** Water-soluble Organoruthenium Complex Salts in Biphasic Catalysis; Synthesis. Annual Conference of the Catalysis Society of South Africa at Langebaan, Cape Town, South Africa, (Nov, 2012)

2. **Poster presentation:** Synthesis and characterization of novel amine complexes $[CpRu(CO)_2]^+$ and $Cp^*Ru(CO)_2]^+$ ($Cp=C_5H_5$; $Cp^*=C_5Me_5$). Inorganic 2013 Conference at Southern Sun Elangeni Hotel, Durban, South Africa (July, 2013)

3. **Poster presentation:** Synthesis and characterization of new 1-aminoalkane complexes of $[CpRu(CO)_2]^+$ and $Cp^*Ru(CO)_2]^+$ ($Cp=C_5H_5$; $Cp^*=C_5Me_5$). The Catalysis Society of South Africa 24$^{th}$ Annual Conference at Wild Coast Sun, Port Edward, South Africa, (Nov, 2013)

4. **Poster Presentation:** Antimicrobial activity of new ruthenium(II) amine complex Salts, $[(\eta^5\text{-}C_5H_5)Ru(CO)_2L]BF_4$ (L = $RNH_2$). 2014 Postgraduate Research Day, (College of Agriculture, Engineering and Science) at UKZN, Westville campus, (Oct, 2014).

5. **Oral Presentation:** New water-soluble $\eta^5$-cyclopentadienyldicarbonyl ruthenium(II) complexes in catalytic oxidation of olefins. Catalysis Society of South Africa 25$^{th}$ Annual Conference at St. George Hotel, Pretoria, South Africa, (Nov. 2014).

Signed: ……

# DEDICATION

*This thesis is dedicated to my beloved son Dennis Ndung'u, and daughter Sharon Wanjiru*

## ACKNOWLEDGEMENT

I wish to express my sincere thanks to all those who made the completion of this work successful.

I wish to express my sincere gratitude to my supervisor Prof. H. B. Friedrich for his guidance, encouragement, devotion and patience throughout my PhD study. Your kindness, enthusiasm and faith in me energized me to strive on even when there seemed to be no hope. Thank you, Prof, for your generosity.

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I gratefully acknowledge the financial support by the NRF, THRIP and the University of KwaZulu-Natal without which it would have been difficult to successfully complete this work.

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Finally, I would like to thank my late parents Mr. Micah Nyawade and Mrs. Apeles Nyawade for their love and support throughout my life, without which, I would not have reached this far.

TABLE OF CONTENTS

# CHAPTER ONE

## 1. Introduction

This thesis focuses on the synthesis, characterization and structural elucidation of $\eta^5$-cyclopentadienyldicarbonylruthenium(II) amine complexes, and their possible application as catalysts in the oxidation of styrene using sodium periodate as the oxidant. Their possible activity as antimicrobial agents against Gram positive and Gram negative bacteria has also been explored. The thesis has been written according to format 4 as stipulated in the guidelines from the College of Agriculture, Engineering and Science. The chapters consist of an overall introduction, discrete research papers and a final discussion. Some of the research papers have been published in internationally recognized, peer-reviewed journals.

Chapter one of the thesis reviews literature about ruthenium as an element and its special characteristics that make it suitable for application in various fields such as medicine and catalysis. Importance and coordination modes of the cyclopentadienyl, carbonyl and nitrogen containing ligands used in this work are briefly discussed. The chapter also gives a brief introduction to the chemistry of $\eta^5$-cylopentadienyldicarbonylruthenium complexes and application of ruthenium complexes in homogenous catalysis with catalytic oxidation of olefins being the main focus. Application of ruthenium complexes in medicine is also reviewed, with possible uses as antimicrobial agents being the main focus. The aim and specific objectives of the project are given at the end of this chapter. The results of the study are presented in chapter two to six in the form of five discrete papers. Each chapter consist of an abstract, introduction, experimental, results and discussion, conclusion and references

Chapter two of the thesis is a published paper on the synthesis, characterization and crystal structure of two polymorphs of a tetrafluoroborate salt of a cationic iodo-bridged $\eta^5$-cyclopentadienyldicarbonylruthenium dimer. The formation of this product during the synthesis of the amine complexes directed the procedure adopted for the synthesis of the ruthenium amine complexes in this work. Chapters three (published paper) and four (manuscript) presents the synthesis and characterization of new, water-soluble 1-aminoalkane complexes of $\eta^5$-cyclopentadienylruthenium(II) and $\eta^5$-pentamethycyclopentadiellruthenium(II) dicarbonyl respectively. The fifth chapter (submitted paper) covers the synthesis and characterization of a

series of new dinuclear diaminoalkane-bridged dicarbonyl(cyclopentadienyl)ruthenium(II) complex salt. The antibacterial activity of the dinuclear complexes synthesized and those of some monouclear ruthenium amine complexes have been determined. The sixth chapter presents the preparation and determination of catalytic activity of cyclopentadienyl ruthenium dicarbonyl complexes of functionalized amine ligands. Finally, the main conclusion of this thesis is presented in Chapter 7. The appendices are presented in a Compact Disk (CD).

### *1.1 Ruthenium*

Ruthenium is a rare transition metal with the symbol $^{101}_{44}Ru$ ([Kr]4d$^7$5s$^1$), and is inert to most chemicals. It was the last of the six platinum group metals to be isolated, and was discovered in 1844 [1]. Ruthenium exhibits characteristics universal to both early and late-transition metals, bringing together desirable properties optimal for catalysis and other applications. For instance, the elements to its left in the periodic table are highly reactive, while those to its right are Lewis acidic in nature and less oxophilic [2]. Ruthenium displays the widest range of oxidation states; from $Ru^{VIII}$ ($d^0$) as in $RuO_4$ [3] and $Ru^{VII}$ as in $RuO^-$ to $Ru^{-II}$ as in $Ru(CO)_4^{2-}$ ($d^{10}$) [4]. Higher oxidation states are stabilized by good σ-donors such as $F^-$, $O^{2-}$ and $N^{3-}$ while low oxidation states are stabilized by effective π-acceptors such as CO and $NO^+$. Ruthenium also displays various coordination geometries in each electron configuration. For instance, ruthenium complexes adopt the trigonal-bipyramidal and octahedral geometries in the primary lower oxidation states of 0, II, and III [4].

The chemistry of ruthenium is of great interest, mainly because ruthenium complexes have a range of valuable features, which include high Lewis acidity, high electron transfer ability, low redox potentials, and ability to form stable reactive metallic species such as metallacycles, oxometals, and metal carbene complexes. Thus such a variety of ruthenium complexes may possibly be utilized in new catalytic reactions, synthetic methods and in pharmaceuticals. Therefore, there is a need to explore the possibility of designing new ruthenium complexes with the potential to catalyze important organic processes, such as oxidation of olefins. Furthermore, they may find application in medicine as antimicrobial and therapeutic agents.

### *1.2 Ruthenium(II) complexes*

A metal complex or a coordination complex is a species which has a central metal atom or ion to which a number of other molecules or ions, referred to as ligands, are bonded by co-ordinate

bonds [5]. The $Ru^{II}$ cation ($[Kr]4d^6$) has empty molecular orbitals into which ligands can donate their lone pairs of electrons and form coordinate bonds.

The most common precursor in the synthesis of ruthenium complexes is the synthetically versatile ruthenium trichloride [6]. Ruthenium complexes can be roughly grouped into oxo, carbonyl, tertiary phosphines, cyclopentadienyl, arenes and dienes, according to their supporting ligands [7,8]. Several ruthenium(II) complexes with nitrogen donor atoms have been synthesized; $[Ru(NH_3)_5N_2]^{2+}$ [9], $[Ru(NH_3)_5NCC_6H_5]^{2+}$ [10], $\eta^5$-$C_5H_5(Ru(CO)(CH_3CN)_2]^+$ and complexes of pyridine derivatives [11-13]. These complexes have multiple applications in many different scientific fields, ranging from pharmaceuticals to catalysis [14-17], hence the great interest in developing organometallic chemistry of ruthenium complexes further.

The ruthenium(II) complexes synthesized in this study mainly contain the carbonyl, cyclopentadienyl and nitrogen containing ligands. A brief discussion of the three types of ligands is, therefore, given.

### *1.2.1 The carbonyl ligand*

Transition metal complexes with coordinated carbon monoxide as a ligand are called metal carbonyls. Bonding of carbon monoxide to transition metals has two components arising from: an overlap of a lone pair of electrons on the carbon atom with empty hybridized d, s, and p orbitals on the metal forming a σ-bond; and π-backbonding or π-back-donation where filled d-orbitals on the metal overlap with an empty π* orbital protruding from the carbon of the CO, forming a π-bond. It is important to note that for π -backbonding to occur, the metal should be in relatively low oxidation state, +2 and below, and must have d-electrons.

The carbonyl group, CO, is an important ligand in organotransition metal chemistry, because it stabilizes transition metal complexes in low oxidation states. The high catalytic activity of carbonyl compounds and their use as precursors in organometallic syntheses can be attributed to the nature of the bonding in low-oxidation state transition-metal carbonyl complexes. Addition or loss of CO to or from a metal centre is a requisite step in many transition metal catalyzed processes [18-20].

Furthermore, the carbonyl group has been shown to have physiological effects that are well described in literature [21-25]. Metal carbonyls are potential CO-releasing molecules (CO-

RMs); coordination complexes such as $\eta^4$-(4-bromo-6-methyl-2-pyrone)tricarbonyliron(0) [26], tricarbonyldichlororuthenium(II) dimer [24], dimanganese decacarbonyl [24] and tricarbonylchloro(glyconato)ruthenium(II) [24] have been shown to promote vasodilatory, cardioprotective and anti-inflammatory activities. Pathogenic bacteria such as Escherichia coli and Staphylococcus aureus are rapidly killed by carbon monoxide delivered through organometallic CO-RMs [27,28]. CO preferentially bound to the ferrous iron of heme protein causes the increased activity of CO against bacteria under anaerobic and aerobic conditions [27,28]. Metal carbonyl compounds have also found application as tracers in carbonylmetalloimmunoassay procedures as an alternative to radioimmunoassay procedures in molecular recognition [29,30], due to the characteristic νCO bands appearing in the 1800–2200 $cm^{-1}$ region, where few other functional groups absorb.

Coordinating the carbonyl ligand to the ruthenium centre in the complexes synthesized in this work was assumed to lead to the formation of potentially effective ruthenium complex catalysts. It was also assumed that the inclusion of the carbonyl ligand would afford complexes that are active antimicrobial and chemotherapeutic agents.

### *1.2.2 The cyclopentadienyl ligand*

The cyclopentadienyl anion, ($[C_5H_5]^-$ (Cp)), on the other hand is a ubiquitous and important ligand [31,32] that is quite inert to most nucleophiles and electrophiles and hence functions solely to stabilize the metal complex. The Cp ligand often bonds to the metal in a $\eta^5$ (pentahapto) fashion by contributing 5 electrons; four from the two double bonds and one electron from the negative charge. Cyclopentadienyl ruthenium complexes mainly exhibit the pseudo-octahedral "piano stool" structure, $CpRuL_n$ (n = 2, 3 or 4) (Fig. 1) with the Cp ligand forming the 'seat' and the ligands forming the 'legs' of the stool. The hybridization of s–p or s–p–d orbitals of the metal has been shown to relate to both donor–acceptor properties and geometry of the $Cp'ML_n$ complexes [33-41].

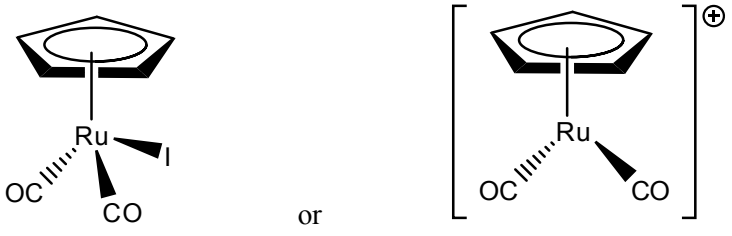
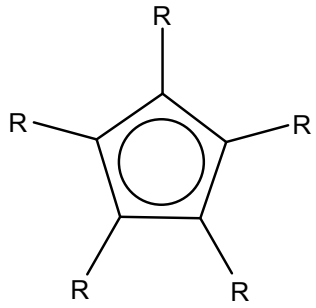



**Figure 1:** Illustration of the piano stool structure of Cp complexes

The steric and electronic properties of the cyclopentadienyl metal complexes can easily be modified by changing the ring substituents, thus making cyclopentadienyl one of the most important ligands in organometallic chemistry. There are a large number of substituted analogues with the pentamethylcyclopentadienyl derivative, denoted by $Cp^*$, being more common, while Cp´ is used as a general abbreviation for Cp and all its derivatives (Fig. 2).




R = H; Cp

R = $CH_3$; Cp*

R = H, $CH_3$, Phenyl etc.; Cp'

**Figure 2:** Cyclopentadienyl ligand and its derivatives

Ruthenium complexes containing the cyclopentadienyl group are important because they can be used as starting materials in organometallic syntheses, and are widely applied in transition metal-catalyzed [42-50], as well as in stoichiometric [51-54] organic syntheses. Catalytic activity of the $\eta^5$-cyclopentadienyl ruthenium complexes ranges from hydrogen transfer to ring closing metathesis [55,56]. The multiple, hence strong bonding of the Cp` fragment relative to the co-ligands in a metal complex, renders the cyclopentadienyl moiety a non-participant in catalytic transformations.

### *1.2.3 Nitrogen containing ligands*

The majority of organic molecules, pharmacophores [57] and proteins in biological systems contain carbon and nitrogen. Microbial, vegetable and animal metabolisms generate amine functionalities found in biogenic molecules. Some biogenic molecules containing the amine functionality are illustrated in Figure 3. Most of the molecules function as regulators of various biological processes in living organisms [58].

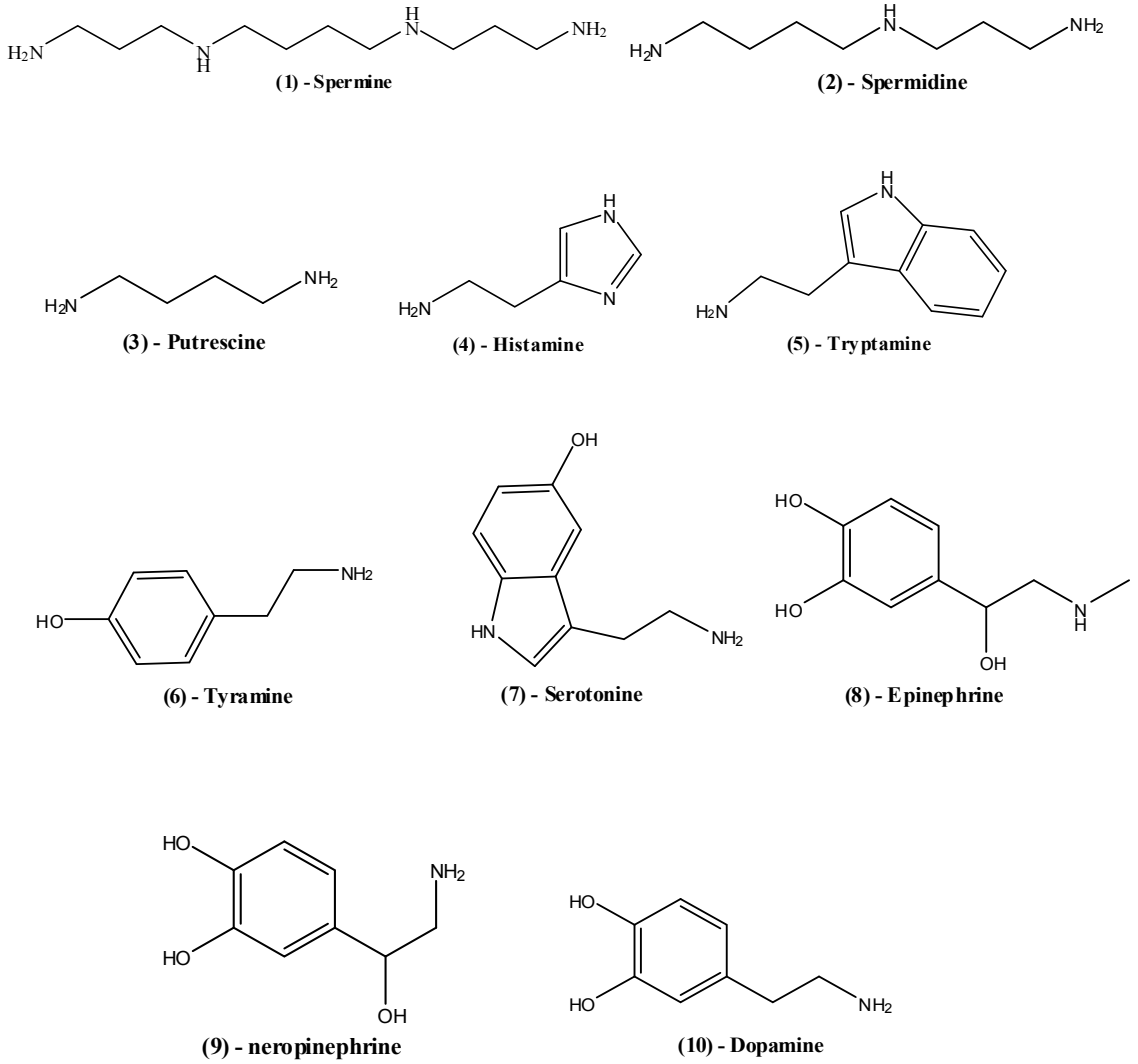



**Figure 3:** Molecules **1-10** are some biogenic amine molecules

Many nitrogen containing compounds have been demonstrated to be important in pharmacology as well as in catalysis. Amine-containing drugs are a very important class of therapeutic agents, with the majority of all drugs containing at least a nitrogen atom in their structure. α,ω-Diaminoalkanes are a significant and versatile class of compounds with significant applications and roles in various fields. For instance in pharmaceutical chemistry, 1,2-ethylenediamine has been shown to be responsible for the action of ethambutol, a front-line drug, in the treatment of tuberculosis (TB) [59,60]. Studies done on anti-tubercular activity of α,ω-diaminoalkanes have shown that long chain α,ω-diaminoalkanes, $H_2N(CH_2)_nNH_2$ (n = 9 – 12) exhibit good activity, in the range 2.5 – 3.12 μg/mL, against Mycobacterium tuberculosis [61]. Another analogue of ethambutol, bis-glycosylated diamino alcohol, has also been shown to demonstrate good activity against the multi-drug resistant (MDR) strain of M. tuberculosis [62]. Diethylcarbamazine

(DEC) (N,N-diethyl-4-piperazine-1-carboxamide) is a synthetic derivative of piperazine used in the treatment of filariasis in humans, dogs and cats. Tertiary amines, as well as secondary amines, such as N-hexylcyclohexylamine, exhibited microfilaricidal response against Acanthocheilonema viteae [63].

Furthermore, the readily available and highly versatile primary amines have emerged as very effective catalysts in asymmetric synthesis. They have exhibited effective catalysis in several enantioselective organic reactions [64,65]. For instance, primary amino acids such as proline are good organocatalysts with the primary amino group providing unique reactivity and stereoselectivity in asymmetric aldol and Mannich reactions [66]. Bidentate primary amines coordinated to metal Lewis acids are efficient catalysts in the direct asymmetric aldol reactions of ketones offering excellent stereoselectivity [67].

Even though the amine functionality has been shown to play a great role in catalysis, pharmacology and physiology, the coordination of simple amine ligands to transition metals is an area that has not been widely studied [68-72]. By combining the catalytic and medicinal properties of the $[CpRu(CO)_2]$ fragment with those of nitrogen containing ligands such as amines, it was hoped that the complexes synthesized in this work would have good catalytic and antibacterial activities. In this study, $\eta^5$-cyclopentadienyldicarbonylruthenium(II) complexes of various primary amines were synthesized and characterized, and their catalytic and antimicrobial activities investigated.

### *1.2.4 The chemistry of η5-cyclopentadienyldicarbonylruthenium(II) complexes*

The cyclopentadienyl metal dicarbonyl fragment, $CpM(CO)_2$, is a common constituent of a large class of complexes. The fragment is commonly denoted as 'Mp', where M varies with the metal; for instance, Rp = $CpRu(CO)_2$ and Fp = $CpFe(CO)_2$. The complexes are fairly stable towards air, moisture and temperature. They can be characterized readily by IR and NMR spectroscopy based on simple spectroscopic features, such as two strong ν(C≡O) absorptions in the region 1800 – 2200 $cm^{-1}$ and a single Cp resonance in the $^1H$ and $^{13}C$ NMR spectra.

Ruthenium complexes containing both cyclopentadienyl and carbonyl ligands have been in existence for more than five decades. The first cyclopentadienyl ruthenium dicarbonyl dimeric complex, $[CpRu(CO)_2]_2$, was synthesized by Fischer and Volger by treating the polymers, $[Ru(CO)_2I_2]_n$ and $[Ru(CO)_2Cl_2]_n$ with sodium cyclopentadienide, NaCp [73]. Since then, the

ruthenium dimer, $CpRu(CO)_2]_2$, has been extensively used as a precursor in the synthesis of $\eta^5$-cyclopentadienyldicarbonylruthenium(II) complexes. The complexes are obtained from the ruthenium dimer either by oxidative or reductive cleavage of the Ru—Ru bond. Reductive cleavage mainly involves monoelectronic reducing agents such as Li, Na and K in THF leading to the anionic complex $[CpRu(CO)_2]^-$, while oxidative cleavage is achieved by the halide ions, X ($Cl^-$, $Br^-$ and $I^-$) leading to the complexes $[CpRu(CO)_2X]$. Treatment of $[CpRu(CO)_2]_2$ with sodium amalgam [74] or potassium amalgam [75] gives the complex anion, $[CpRu(CO)_2]^-$. The reaction of the complex anion $[CpRu(CO)_2]^-$ with $C_6F_5COCl$ afforded the para-disubstituted diruthenium complex, $[CpRu(CO)_2C_6F_4CORu(CO)_2Cp]$. The propionyl complex $CpRu(CO)_2COC_2H_5$ was prepared by treating the sodium salt, $Na^+[CpRu(CO)_2]^-$, with propoinyl chloride in THF [75]. The complex $[CpRu(CO)_2Me]$ was synthesized by refluxing $K^+[CpRu(CO)_2]^-$ and methyl iodide in THF at 45 °C for several days [76]. Brookhart and co-workers [77] used the anionic complex, $[CpRu(CO)_2]^-$ to synthesize ruthenium cyclopropylcarbene complexes shown in Figure 4.

The dimer $[CpRu(CO)_2]_2$ can also be synthesized by refluxing cyclopentadiene and $Ru_3(CO)_{12}$ in heptanes [78,79]; depending on the workup, $CpRu(CO)_2H$ is synthesized by a similar procedure. Shvo and co-workers used the complex $Ru_3(CO)_{12}$ as a precursor in the synthesis of the dimeric hydrogenation catalysts, $[(\eta^4\text{-}Ph_4C_4CO)(CO)_2Ru]_2$ and $[(\eta^4\text{-}Me_2Ph_2C_4CO)(CO)_2Ru]_2$ (Fig. 5) [80].

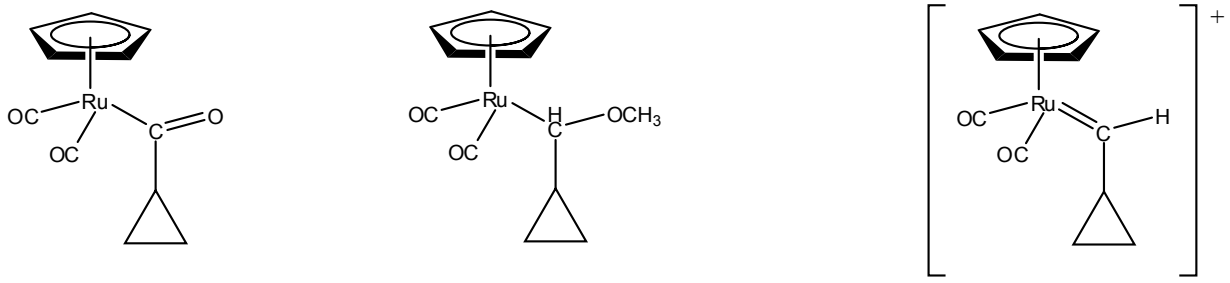



**Figure 4:** Ruthenium cyclopropylcarbene complexes

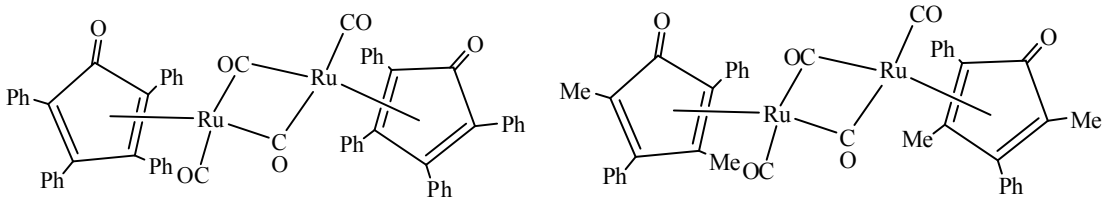


**Figure 5:** Shvo's hydrogenation catalysts

The dimer $[CpRu(CO)_2]_2$ has been widely used as a precursor for the synthesis of the halo cyclopentadienyl dicarbonyl ruthenium complexes, $CpRu(CO)_2X$ and $[CpRu(CO)_2]_2X$ (X = Cl, Br or I) (Equations 1 and 2) [81].

$$[CpRu(CO)_2]_2 + X_2 \xrightarrow[RT;\ 1\ h]{CH_2Cl_2 \text{ or } CHCl_3} 2CpRu(CO)_2X \qquad \text{Equation 1}$$

$$[CpRu(CO)_2]_2 + X_2 \xrightarrow[RT;\ 1\ h]{\text{benzene or toluene}} [CpRu(CO)_2]_2X \qquad \text{Equation 2}$$

These halide complexes, $CpRu(CO)_2X$, have been extensively used as precursors in the synthesis of both neutral and cationic complexes of the type $CpRu(CO)_2L$ and $[CpRu(CO)_2L]Y$ (L = ligand; Y = counter anion) respectively. Jungbauer and Behrens synthesized several complexes using $CpRu(CO)_2Cl$ as a precursor and $AlCl_3$ as the halogen abstractor, as illustrated by Equation 3 [82]. Other syntheses by Jungbauer are illustrated in Equations 4 and 5

$$CpRu(CO)_2Cl + n\,AlCl_3 + L \xrightarrow[C_6H_6]{25\ ^oC\ -\ 80\ ^oC} \{[CpRu(CO)_2]_nL\}(AlCl_4)_n \qquad \text{Equation 3}$$

$$n = 1: \quad L = CH_3CN, \text{ propene, cyclohexene;} \quad n = 2: \quad L = Ph_2PCH_2CH_2PPh_2$$

Reaction of the complexes with $NH_4PF_6$ or $NaBF_4$ gave the corresponding complex salts, $\{[CpRu(CO)_2]_nL\}(PF_6)_n$ or $\{[CpRu(CO)_2]_nL\}(PF_6)_n$ respectively.

$$CpRu(CO)_2Cl + NH_3 \xrightarrow[\text{Liquid } NH_3]{-\ 33\ ^oC} [CpRu(CO)_2NH_3]Cl + CO \qquad \text{Equation 4}$$

$$CpRu(CO)_2Cl + L \xrightarrow[C_6H_6]{60 - 70\ ^oC} [CpRu(CO)_{2-n}L]Cl + nCO \qquad \text{Equation 5}$$

n = 0: L = PEt; n = 1: L = $Ph_2PCH_2CH_2PPh_2$

It is worth noting that very few $CpRu(CO)_2$ complexes with simple nitrogen containing ligands have been reported. In the nitrogen-containing ruthenium complexes, $[CpRu(CO)_2NH_3]^+$ [82], $[CpRu(CO)_2CH_3CN]PF_6$ [82,83] and $[CpRu(CO)_2(NCO)$ [84], the ligand is coordinated to the metal through the nitrogen atom, whereas in $[CpRu(CO)_2(CONHNH_2)]$ [84] and the quaternary ammonium salt, $\{CpRu(CO)_2[CH_2CH_2(NH_3)^+]\}PF_6$ [85], the ligand is not coordinated through the nitrogen atom. The $\eta^5$-cyclopentadienyldicarbonylruthenium(II) complexes in which primary amines are coordinated to the ruthenium centre via the nitrogen atom were reported by us for the first time [86].

The $\eta^5$-cyclopentadienyldicarbonylruthenium(II) complexes of various primary amines synthesized in this study are soluble in water and were used as catalysts in the oxidative cleavage of styrene. Their antimicrobial activity against selected Gram-positive and Gram-negative bacteria was also tested. In the next sections, a brief review of the use of ruthenium complexes in both catalysis and medicine is given. The importance of water solubility of organometallic complexes is discussed.

### *1.3 Water soluble organometallic complexes*

Water is the most desirable solvent in catalysis because it is cheap, abundant, non-flammable, and nontoxic. There has been great interest in water-soluble organometallic complexes due to their usefulness in aqueous biphasic catalysis [87,88]. The use of biphasic catalysis allows for utilization of water as a co-solvent, hence, it is important in designing green chemical processes. Since the amine group is hydrophilic, including them in the complex may make the organometallic species water soluble. Water is also very important in biological systems, since it is the main solvent. Solubility of organometallic compounds in water is a major prerequisite for innovations in biomedicine [89], bioorganometallic chemistry and organometallic radiopharmaceuticals. Aqueous solubility is one of the important properties required for early stages of effective drug delivery, hence the need to explore the possibility of synthesizing water soluble complexes. Furthermore, due to the growing interest in green chemistry, the desire to use aqueous phase catalysis has made the development of water soluble organometallic

compounds vital in both the laboratory and industry. The synthesis of a series of 1-aminoalkane and α,ω-diaminoalkane complexes of $\eta^5$-cyclopentadienyldicarbonyliron(II) was recently reported [68]. The amino group on the hydrocarbon chain renders these complexes soluble in water by virtue of hydrogen-bonding. The 1-aminoalkane complexes were shown to react with sodium salts such as $NaBPh_4$ and NaI in aqueous media to give the respective $BPh_4^-$ and $I^-$ salts [70].

### *1.4 Ruthenium complexes in catalysis*

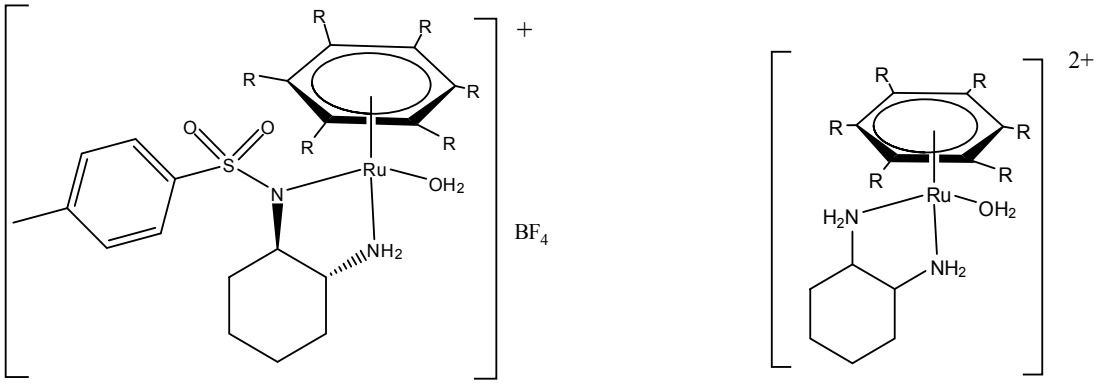
A catalyst is a substance that is able to accelerate a chemical reaction by providing an alternative reaction pathway with significantly lower activation energy as compared to the non-catalyzed process [90]. Activation energy for a reaction in organometallic catalysis decreases through coordination of the substrates to the transition metal centre, thus promoting the reaction [91-94]. Catalysis is significant in the chemical industry because it contributes both to its economical success and environmental sustainability. Catalysis can be categorized as homogeneous or heterogeneous, depending on their relationship to the phase of the reaction in which they are involved. If a catalyst is in the same phase as the components of the reaction it catalyses, it is homogenous, whereas one in a different phase from the components of the reaction it is catalyzing is heterogeneous. Homogeneously catalyzed reactions have improved activity due to their monomolecular nature, high selectivity (i.e. regioselectivity, enantiomeric excesses), and their ability to avoid mass transfer limitations, thus favouring lower temperature conditions. The main disadvantage of homogeneous catalysis is the difficult and costly catalyst separation and recovery due to homogeneous nature of the solution. Contamination of the product by residual catalyst or metal species is also a challenge. Biphasic solvent systems have been developed in an effort to improve recovery and recyclability of selective homogeneous catalysts, as well as minimize industrial waste streams [95-97]. An aqueous biphasic system is a typical example where catalyst recovery can be achieved by maintaining an aqueous catalyst-rich phase separate from the substrate containing non-polar organic phase. The two phases can be separated by decantation, resulting in no loss of catalyst. The aqueous layer can be recycled many times yielding high catalytic turnover with little metallic contamination of the product. This aspect has made the water-soluble organometallic complexes more attractive due to their utility in aqueous biphasic catalysis.

Organometallic complexes are mainly homogeneous catalysts and enhance conversion as well as product selectivity by accelerating just one of the competing reaction sequences when

alternative routes exist [98-100]. Ruthenium complexes have been reported as catalysts in reactions such as oxidation, isomerisation, carbon–carbon bond formation, racemisation of alcohols and amines, polymerization, olefin metathesis and nucleophilic addition to multiple bonds [101-105].

### *1.4.1 Homogenous catalysis and water soluble complexes*

Application of water-soluble organometallic complexes in catalysis has continued to attract interest because the process is environmentally friendly, product separation is simple and selectivity in aqueous media is pH dependent [88]. The recycling of aqueous organometallic catalysts represents a fundamental application of the core principle of green chemistry and sustainable technology through the reduction of waste streams and remediation and the combination of atom economical catalytic chemistry with water. The solubility of organometallic complexes in water is usually achieved by introduction of polar substituents in their structures [106]. The most commonly used polar substituents are hydroxyl and amino functionalities, as well as ionic groups such as sulfonate, carboxylate and ammonium. Nitrogen coordinated water soluble organometallic complexes have also been shown to be active aqueous biphasic catalyst. For instance, the cationic ruthenium complexes **11** and **12** are effective catalysts for enantioselective transfer hydrogenation of aryl ketones [107], while complexes **13** and **14** have been shown to be effective catalysts in transfer hydrogenation of acetophenone (Fig. 6) [108]. Biphasic catalysts can be pH dependent [109,110] and counter anions such as $PF_6$ and $BF_4$ have been shown to boost the performance of ruthenium catalyst [109].




R = H (**11**); R = Me (**12**)

R = H (**13**); R = Me (**14**)

**Figure 6:** Water-soluble nitrogen coordinated ruthenium complexes, **11**, **12**, **13** and **14**, as biphasic catalyst

### *1.4.2 Catalytic oxidation of organic syntheses*

Oxidation catalysis represents the core of a variety of chemical processes for producing bulk and fine chemicals. Oxidation catalysis based on ruthenium, a powerful and useful synthetic tool, selectively affords oxygenate products both in homogeneous and heterogeneous processes [111,112]. Ruthenium complexes have been shown to selectively catalyse a large variety of oxidative conversions, including the generation of molecular oxygen from water [113-115], the dihydroxylation of olefins [50,116], oxidative cleavage of olefinic double bonds [117,118], the oxidative dehydrogenation of alcohols to carbonyls [117,118] and the asymmetric epoxidation of alkenes [119,120]. The ability of ruthenium complexes to catalyze a great variety of oxidation processes is based on ruthenium's wide range of oxidation states, choice of suitable co-ligands, and a generally favourable balance of kinetic lability and stability. Co-ligands used can lead to changes in the redox characteristics of the ruthenium centre and, hence, adjust the oxidation properties of the ruthenium complexes as catalysts. Some substituted $\eta^5$-cyclopentadienyldicarbonyl ruthenium complexes used in the catalytic oxidation of amines are illustrated in Figure 7.

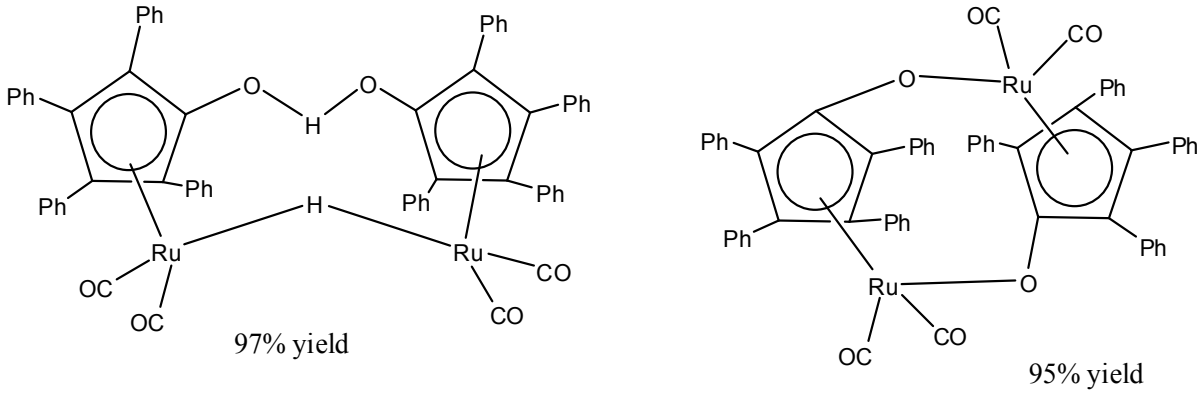


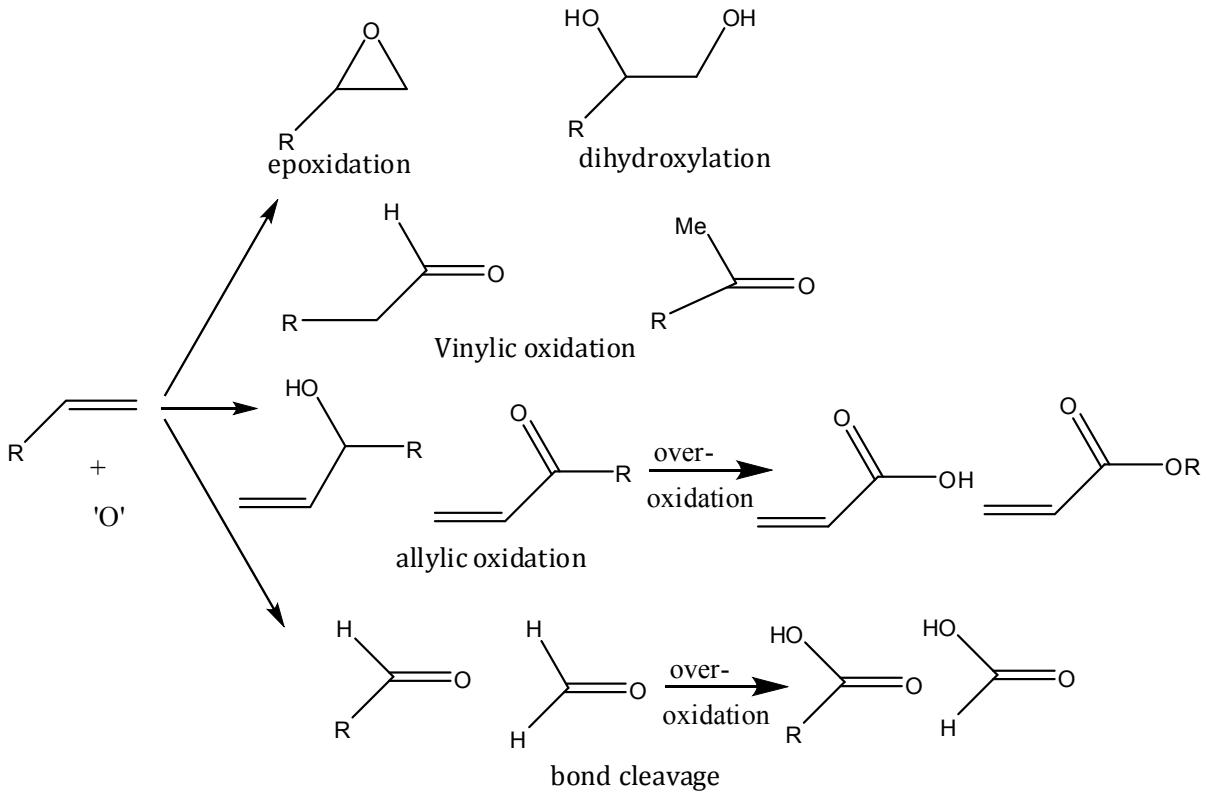

**Figure 7:** $\eta^5$-Cyclopentadienyldicarbonyl ruthenium complexes used in catalytic oxidation of amines

Typical examples of ruthenium complexes that have demonstrated good catalytic activity in oxidation processes are summarized in Table 1.

#### 1.4.2.1 Olefin oxidation

Metal catalyzed oxidation of terminal olefins gives rise to a variety of products as illustrated in Scheme 1 [121]. This discussion is mainly focused on the oxidative cleavage of olefins.

The oxidative cleavage of a C—C double bond involves splitting of the double bond and insertion of oxygen into the two fragments (Scheme 1). The initial oxidation products of terminal alkenes are two aldehydes, while tertiary alkenes yield both an aldehyde and ketone. Aldehydes can be over-oxidized to carboxylic acids, while ketones are not oxidized. Oxidative cleavage, therefore, provides access to intermediates suitable for sequential reactions, or directly affords valuable products by adding functionality to the substrate.




**Scheme 1:** Products of metal-catalyzed oxidation of terminal alkenes

**Table 1:** Oxidation reactions catalyzed by Ru complexes

| Catalyst | Co-oxidant | Oxidation reaction catalysed | Conditions | Ref. |
|---|---|---|---|---|
| $[Ru^{III}(bda)(mmi)(OH_2]CF_3SO_3$ ($H_2bda$ = 2, 2'-bipyridyl-6,6' –dicarboxylic acid; mmi = 1, 3-dimethylimidazolium-2-ylidene) | $Ce^{IV}$ or electrochemically | water oxidation | | [113,115] |
| $[Ru^{III}(amp)(bipy)(H_2O)]^+$ ($H_2amp$ = N-(2-hydroxyphenyl)salicyldimine; bipy = 2,2`-bipyridyl) | t-BuOOH | benzene to phenol | $CH_2Cl_2$; RT | [122] |
| $[Ru^{II}(amp)(bipy)Cl]$ | t-BuOOH | cyclohexene to cyclohexene-1-ol, cyclohexane to cyclohexanol and cyclohexanone, stilbene to stilbene epoxide and benzaldehyde | $CH_2Cl_2$; RT Phase transfer catalyst (benzyltributylammoniumchloride) | [123] |
| $RuL(CO)_2Cl_2$, $[RuL(CO)_2L'_2]^{2+}$ and $[RuL(CO)_2ClL']^+$ (L = bipyridine (bpy), phenanthroline (phen), biquinoline (biq) and L' = pyridines, 4-chloropyridine, 4 – methoxypyridine) | PhIO | epoxidation of olefins | $(CH_3)_2CO/H_2O$; 25 °C | [124] |
| trans-$Ru^{VI}(tmp)(O)_2$] (tmp = 5, 10, 15, 20 – tetramesitylporphyrin) | Air | dehydrogenation of primary and secondary amines | | [125] |
| Ruthenium(II) porphyrin complexes | NMO or $O_2$/air | alkenes to aldehydes (scheme 1) | | [126] |
| $RuL_2$ (L = 1, 10-phenanthroline, 8-hydroxyquinoline and 2, 2`-bipyridine) | PhIO | benzylic and aliphatic alcohols to corresponding aldehydes and ketone | MeCN; RT | [127] |
| Figure 7 | Air | oxidation of amines to nitriles and imines | Toluene; 110 °C | [128] |

Oxidative cleavage pathways discussed in literature can be summarized into two main categories: (i) dihydroxylation followed by cleavage with $NaIO_4$ or other oxidants [80] or (ii) ozonolysis which involves direct cleavage of the olefin into a variety of functionalized products depending on the workup conditions [102-104]. The direct oxidative cleavage of olefinic double bonds is conventionally performed at industrial level by ozonolysis to convert alkenes into aldehydes or carboxylic acids [129] upon oxidative or reductive workups respectively. The problem with ozonolysis is the dangerous and unstable nature of ozone, the oxidant, which necessitates use of high-technology equipment, which increases the overall cost [114,130]. The oxidative cleavage can also be achieved by several stoichiometric oxidants, such as m-chloroperbenzoic acid (mcpba) used for cleavage of diarylethylene derivative to ketones [64] and $PhIO/HBF_4$ (1:1 equiv) which affords aldehydes selectively [131].

Several transition metal-containing compounds have been used as stoichiometric oxidants in the oxidative cleavage of olefinic double bonds but there are drawbacks to their usage. Stoichiometric amounts of $KMnO_4$, for instance, oxidises olefins to aldehydes [132] or carboxylic acids [133-135], but the organic substrates formed are often poorly soluble in the aqueous reaction medium. It is also worth noting that $KMnO_4$ cannot be used in catalytic amounts due to the irreversible precipitation of $MnO_2$ after oxidation of the substrate. On the other hand, chromyl chloride, $CrO_2Cl_2$, [136] oxidises styrene into benzaldehyde and phenylacetaldehyde [137], but since such chromium salts are known to be very toxic, their use is discouraged.

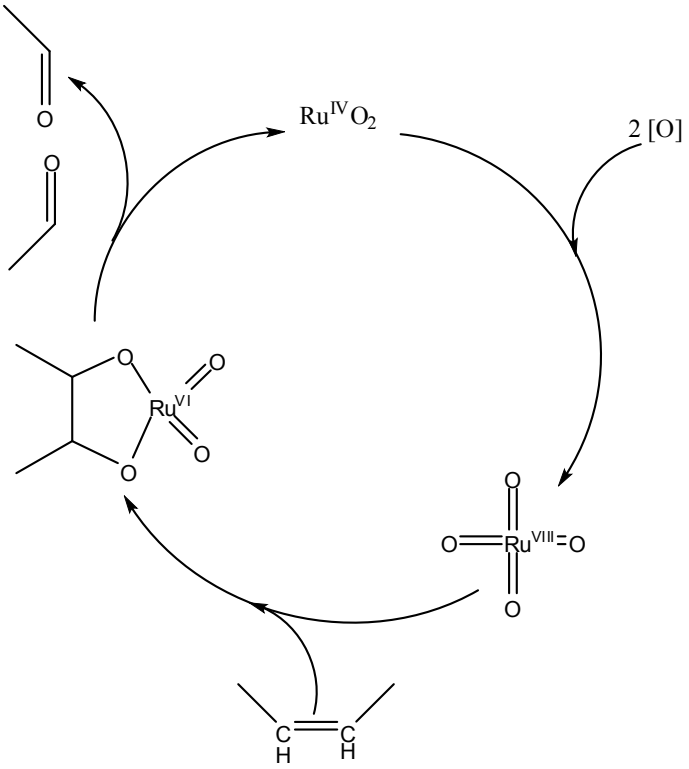
The challenges encountered in using ozone and stoichiometric amounts of the transition metal compounds inspired research into the use of simple ruthenium salts and complexes as catalysts for the oxidative cleavage of olefinic double bonds. $RuO_4$ has been used as a selective stoichiometric oxidant for the conversion of alkenes to aldehydes [3,138]. Simple ruthenium salts, $RuO_4$ and $RuCl_3$. $nH_2O$, have been widely used as catalysts in the oxidative cleavage of the olefinic double bond [139-141]. The oxidation of cyclohexene to adipic acid, by stirring a solution of cyclohexene in $CH_2Cl_2$ with an aqueous solution of $RuCl_3.nH_2O$ and NaOCl, was reported [139]. Carlsen and co-workers reported the use of $RuCl_3/NaIO_4$ for the oxidative cleavage of alkenes to carboxylic acid with the $CCl_4$-MeCN-$H_2O$ solvent system [140]. $RuCl_3$, 1.5 equiv. oxone and 4.7 equiv. $NaHCO_3$ in the $MeCN/H_2O$ solvent system selectively cleave styrene and derivatives to aldehydes instead of carboxylic acid [141]. $RuO_2$, formed as an intermediate product when $RuCl_3$ is used as the catalyst, unlike $MnO_2$, is soluble in solvents such as $CCl_4$ or MeCN and can be re-oxidized to $RuO_4$ by $NaIO_4$ [142] or NaOCl [140].

Catalytic amounts of $RuO_2.2H_2O$ and 2-6 equiv. $NaIO_4$ in $CCl_4/H_2O$ were used to cleave electron poor cyclic enolic C=C bonds on the β-position to aldehydes in 35-95% yield [143].

The use of catalytic amounts of ruthenium complexes in the oxidative cleavage of olefins is more advantageous than the use of salts, because it reduces the levels of toxicity of the metal and improves selectivity towards the cleavage products, while preventing side reactions such as epoxidation, dihydroxylation or allylic oxidation. The co-ligand coordinated to the metal plays a major role in improving the catalytic activity as well as selectivity of the catalyst. Several ruthenium complexes, as catalysts, have demonstrated good selectivity to C—C bond cleavage oxidative products in oxidation reactions. The complex cis-$[RuCl_2(bipy)_2].2H_2O$, has been used in catalytic oxidative cleavage of alkenes to acids with $IO(OH)_5$ as co-oxidant as well as chemo-selective degradation of aromatic rings to acids with $NaIO_4$ as a co-oxidant, in the $CCl_4$-MeCN-$H_2O$ biphasic solvent system [117]. $[Cis\text{-}Ru(II)(dmp)_2(H_2O)_2]^{2+}$ (dmp = 2, 9 – dimethylphenanthroline) was used as a catalyst in the oxidative cleavage of terminal alkenes to aldehydes using $H_2O_2$ as the oxidant in acetonitrile at 55 °C [118]. It is worth noting that research into the possible use of ruthenium complexes as catalysts in the oxidative cleavage of C—C double bonds has not been extensively done, despite the fact that they show excellent activity and selectivity.

### 1.4.2.2 Mechanism for oxidative cleavage of olefinic double bond

Simple ruthenium compounds, such as $RuCl_3.nH_2O$ and $RuO_2$, have been shown to catalyse oxidative cleavage of olefinic double bonds through the formation of $RuO_4$ as the main oxidant. $RuO_4$ catalyzed oxidation has been proposed to proceed through the formation of a ruthenium(VI) diether (Scheme 2) which is oxidatively cleaved to give an aldehyde [115,144,145]. After coordination of the alkene, a metal-dioxyethane moiety, a metaldiether, is formed via a 3 + 2 pericyclic reaction (Scheme 2). A sufficient lifetime of the diether is crucial, as its rearrangement yields the desired aldehydes, while hydrolysis causes the formation of diols. $RuO_4$, therefore, shows high selectivity towards cleavage products because the reaction mechanism does not involve epoxidized or dihydroxylated intermediates.




**Scheme 2:** Mechanism for oxidative cleavage of olefin carbon-carbon double bond

Most ruthenium complexes have also been demonstrated to catalyze oxidation processes through formation of an oxo-ruthenium species intermediate as the oxidant [122,146,147]. For instance, the high valent ruthenium oxo-species, $[Ru^{V}(amp)(bipy)O]^{+}$ ($H_2amp$ = N-(2-hydroxyphenyl)salicyldimine; bipy = 2,2`-bipyridyl) is formed during the oxidation process catalyzed by $[Ru^{III}(amp)(bipy)(H_2O)]^{+}$ and $[Ru^{III}(amp)(bipy)Cl]$ [123].

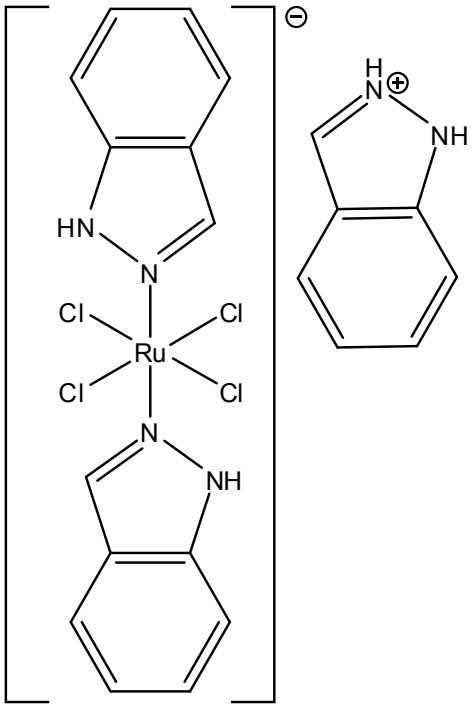
### *1.5 Ruthenium complexes in medicine*

The stability of different oxidation states of ruthenium and, thus, its redox properties are influenced by the coordination environment [148,149]. The activity of ruthenium compounds as drugs depend on the oxidation state, the ligand, as well as their stability in highly acidic and alkaline environments. The toxicity of ruthenium containing drugs are low because, ruthenium is able to mimic iron in the mechanism exploited by the body for non-toxic transportation of iron, i.e. by binding to biomolecules [150]. The ability of the body to catalyse reduction and oxidation reactions in different physiological environment is dependent on the redox potential between the different oxidation states of ruthenium, $Ru^{II}$, $Ru^{III}$ and $Ru^{IV}$, accessible under the

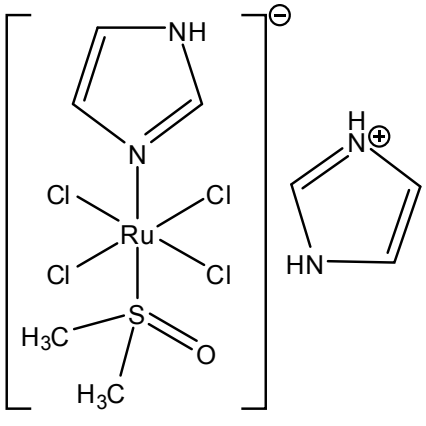
physiological conditions [150]. Furthermore, the physiological environment altered by the biochemical changes that accompany disease facilitates the selective activation of ruthenium compounds in the diseased tissues [150]. Ruthenium complexes have been used as immunosuppresants, antimicrobials [16, 71,125,151,152], antibiotics, nitric oxide scavangers [150] and anticancer drugs [112,113,131]. They have also demonstrated DNA binding [153,154], and chemiluminescence [155].

### *1.5.1 Ruthenium complexes as chemotherapeutic agents*

For a long time, platinum-based compounds have been used as chemotherapeutic agents in to treat solid tumors, such as ovarian and testicular carcinomas [156]. However, the renal, neurologic, gastroenterologic, and marrow toxicity, as well as cancer cells resistance to the platinum-based drugs has triggered the search for new metal-based antitumor drugs, which are more effective and with less side effects [150,157]. Ruthenium, gold and osmium compounds have received great attention as alternatives to platinum compounds [158]. Ruthenium complexes have received greater attention and are extensively studied where two of them, NAMI-A and KP1019/KP1339 (Figure 8), successfully entered clinical trials.




KP1019




NAMI-A

**Figure 8:** Structural formulae of the ruthenium-based chemotherapeutic agents, KP1019 and NAMI-A

NAMI-A, ImH[Ru(Im)(dmso)$Cl_4$] (Im=imidazole), is a chemotherapeutic agent that demonstrates low toxicity, high selectivity and efficacy for solid tumour metastasis at pharmacologically active doses [159-161]. It does not affect primary tumor growth [162]. Contrary to earlier reports that NAMI-A does not exhibit cytotoxicity against tumour cells in vitro [163], recent studies have shown that it induces potent and selective cytotoxic effects on a few leukaemia cell lines [164]. The ruthenium complex, trans-[tetrachlorobis(1H-indazole)ruthenate(III)] KP1019, is also a hopeful chemotherapeutic agent that has demonstrated ability to reduce the size of tumours in rats [165], triggers apoptosis in vitro [166], is non-toxic at any dose administered with about 80% of the patients improving or stabilizing [165] and is also effective against cancer cell lines that are highly resistant to other chemotherapeutic agents [167]. Ruthenium complexes, therefore, are a promising alternative to platinum-based antitumor drugs [168-170].

The cyclopentadienyl and p-cymene ruthenium(II) complexes have been shown to exhibit anti-tumour activity [171-173]. The piano-stool complexes, such as, RAPTA-C [Ru($\eta^6$-p-cymene)$Cl_2$(PTA)](PTA=1,3,5-triaza-7-phosphatricyclo-[3.3.1.1]decanephosphine) [174], best represent this class of compounds. They have properties, similar to those of NAMI-A, that inhibit metastasis process at low in vitro anticancer activity [175]. New research findings have revealed that a new ruthenium compound, [($\eta^6$-1,3,5-triisopropylbenzene)RuCl(4-methoxy-N-(2-quinolinyl-methylene)aniline)]Cl has anticancer activity against ovarian cancer, breast cancer, and colorectal cancer cell lines [170].

### *1.5.2 Antimicrobial and antimycobacterial agents*

Bacteria are capable of rapidly developing resistance to known antimicrobial drugs as well as to new drugs based upon analogues of known scaffolds. Noteworthy, bacterial resistance to antimicrobial drugs is a threat to humans worldwide [176] and, therefore, requires urgent intervention. The increased rate of bacterial resistance and need to eradicate the bacteria has triggered increased interest in the development of new classes of antimicrobial agents [177] that can evade the bacterial mechanisms of resistance developed against the antimicrobial agents in clinical use. The Infectious Diseases Society of America (IDSA) 2009 update [176] indicated that "drug resistance by the 'ESKAPE' pathogens; **E**nterococcus faecium, **S**taphylococcus aureus (S. aureus), **K**lebsiella pneumoniae, **A**cinetobacter baumanii, **P**seudomonas aeruginosa (P. aeruginosa) and **E**nterobacter species is of global concern". Methicillin-resistant S. aureus (MRSA), fluoroquinolone-resistant P. aeruginosa and vancomycin-resistant Enterococcus

(VRE) show increasing rates of infection [178]. There is, therefore, a need to develop new classes of antibacterial agents that may evade the mechanisms of resistance developed by the bacteria against the antimicrobial agents currently in clinical use.

The mycobacterium tuberculosis (MTB), which causes the infectious tuberculosis (TB) disease, is another bacterial strain that is a major threat to human life. The rapid spread of the MTB strain that is resistant to at least isoniazid and rifampicin, known as multidrug resistant TB (MDR-TB), has been a challenge in recent years. In 2011, there were up to 400,000 estimated cases of multidrug-resistant TB (MDR-TB) among notified TB patients with close to 10% of all MDR cases being extensively drug-resistant (XDR-TB), meaning they are also resistant to two of the key drugs used as a part of second-line regimens [179]. Thus, there is a great need to develop new antimycobacterial agents that can act fast while providing more effective treatment against multidrug resistant (MDR), extensive drug resistant (XDR) and latent tuberculosis infections [180]. Currently, two approaches are used in the development of anti-TB drug [181]. Analogues of existing drugs can be synthesized with the aim of reducing the drug administration period and improve TB treatment, or, search for new structures that MTB has never encountered [182]. These approaches are also applicable to the development of other antimicrobial agents.

Transition metal complexes have been successfully used as anticancer agents [183-185], and this has triggered immense interest in metal complexes as antimicrobial agents [12,13,186,187]. Dwyer and co-workers were the first researchers to show that the ruthenium and iron complexes, polypyridyl mononuclear tris(bidentate)-ruthenium(II) and -iron(II) complexes, e.g. $[Ru(Me_4phen)_3]^{2+}$ ($Me_4phen$ = 3,4,7,8-tetramethyl-1,10-phenanthroline), have potential antibacterial activity [151,188]. Their findings have inspired immense interest and research in the possible use of ruthenium complexes as antimicrobial agents. Based on Dwyer's findings, research on ruthenium complexes as potential antimicrobial agents has been mainly focused around polypyridyl ligands [12,13,189]. Li and co-workers synthesized and demonstrated that the inert flexibly-linked dinuclear ruthenium(II) complexes, $[\{Ru(phen)_2\}_2\{\mu\text{-bbn}\}]^{4+}$ {Rubbn; phen = 1,10-phenanthrolin and bb = bis[4(4′-methyl-bipyridyl)]-1, n = alkane (n = 2, 5, 7, 10, 12, 16)}, are potential antimicrobial agents against an array of Gram-positive and Gram-negative bacteria [152,190]. Pandrala and co-workers synthesized a series of polypyridyl-ruthenium(II) complexes, $[\{Ru(tpy)Cl\}_2\{\mu\text{-bbn}\}]^{2/4+}$ {Cl-Mbbn; tpy = 2,2′:6′,2′′-terpyridine; and bbn = bis[4(4′-methyl-2,2′-bipyridyl)]-1,n-alkane (n = 7, 12 or 16)} and demonstrated that $ClRubb_{12}$ is active and bactericidal against the Gram-positive and Gram-negative bacteria

tested. Another ruthenium pyridyl complex with a labile chlorido ligand was reported to be active against bacteria [16]. Lam et al. synthesized ruthenium(II) bis(2,2′-bipyridyl) complexes containing N-phenyl-substituted diazafluorenes and demonstrated their potential antimicrobial activity against the Methicillin-Resistant S. aureus [191]. The binuclear ruthenium(II) carbonyl complexes, [{RuX(CO)($EPh_3$)$_2$}$_2$L] (where X=H or Cl; E = P or As and L = dibasic tetradentate diacetyl resorcinol (H2-DAR)) were shown [192] to be better inhibitors of the growth of the Gram positive S. aureus, and the Gram-negative E. coli and K. pneumoniae than the free ligand. The Ruthenium(II) complexes, $[Ru(dmb)2IIP]^{2+}$, {dmb is 4,4′-dimethyl-2,2′-bipyridine and IIP is 2-(1H-indol-3-yl)-1H-imidazo[4,5-f][1,10-phenanthroline}, have also demonstrated potential antibacterial activities against E. coli and S. aureus by Tweedy's chelation theory [193].

Non-pyridine containing ruthenium complexes have also been shown to be active against a number of bacteria. For example, thiosemicarbazone ruthenium complexes have been shown to exhibit antimicrobial activity against S. aureus, B. Cereus, E. faecalis, S. typhimurium, Proteus vulgaris and Vibrio cholera [194]. Pavan and co-workers synthesized a series of ruthenium(II) phosphine, diimine/picolate complexes [195] and demonstrated their activity against mycobacterium tuberculosis (MTB) [196,197]. They also showed that the ruthenium complexes were more active against MTB than the free ligand [198].

## *1.6 Iron complexes*

### *1.6.1 A survey of η5-cyclopentadienyldicarbonyl iron (II) complexes*

Compounds containing the iron fragment $CpFe(CO)_2$ (Cp = $\eta^5$-$C_5H_5$) have been extensively studied [199-201] since the discovery of $[CpFe(CO)_2]_2$ [202]. Some of the most recent contributions towards the understanding of the chemistry of iron complexes containing the $CpFe(CO)_2$ fragment were made by M'thiruaine et al. [68-72]. They reported the synthesis of the etheral complex $[CpFe(CO)_2O(CH_2CH_3)]BF_4$ and its application as a precursor in the synthesis of the iron amine complexes of the type $[CpFe(CO)_2L]BF_4$, (L = n-alkylamine, α,ω-diaminoalkanes, N-heterocyclic ligands and aromatic amines). It is worth noting that the potential activity of these complexes in catalysis and as antimicrobial agents has not been tested.

### *1.6.2 Iron complexes in catalysis*

The ease with which the oxidation states of iron catalysts are interchangeable and their unique Lewis acid character enables them to catalyse a variety of synthetic transformations; rearrangements, hydrogenations, substitutions, cycloadditions, coupling reactions, reductions, polymerizations, oxidations, isomerizations, and additions. Low-valent α-diimine iron complexes have been demonstrated as good catalysts in the hydrogenation of various C—C double and triple bonds [203-206]. In addition to hydrogenation of the olefinic double bond, Casey and Guan reported the first efficient iron complex (Fig. 9) catalysed $H_2$-hydrogenation of ketones, imines aldehydes and diketones [207]. The catalyst has some structural features similar to the well-known Shvo hydrogenation catalyst (Fig. 5) [80].

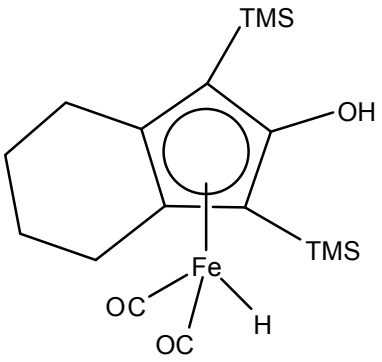



**Figure 9:** Iron complex catalyst for the hydrogenation of ketones, aldehydes and ketones

Catalytic oxidation of cycloalkanes and alkylarenes with catalytic amounts of iron salts was reported by Bolm and co-workers [208,209]. Selective C−H oxidation of ethyl benzene to acetophenone and traces of phenylethanol occurred in the presence of ligand-free iron(II) chloride salts and mild reaction conditions. Epoxidation of olefins by hydrogen peroxide have also been achieved in the presence of iron(II) chloride, pyridine-2,6-dicarboxylic acid (H2pydic), and a chiral diamine as a three-component catalyst [210]. 1,2-disubstituted aromatic olefins were epoxidized with enantiomeric excesses of up to 97% ee. Bis(imino)pyridine iron pre-catalysts have been shown to catalyze the hydroxylation of aldehydes and ketones [211]. Furthermore, iron-based catalysts have been shown to be highly active and selective in the oligomerization of ethylene to linear α-olefins [212,213].

In this study, therefore, the antimicrobial and catalytic activity tests on some of the Cp´ iron complexes, $[Cp´Fe(CO)_2L]^+$, have been done alongside the $\eta^5$-cyclopentadienyldicarbonyl-ruthenium(II) amine complexes synthesized and characterized herein.

### *1.7 Hypothesis*

Ruthenium complexes have been reported as ideal catalysts for many organic syntheses. Amines have been reported to be effective catalysts and have antimicrobial activities as well. Furthermore, the medicinal properties of various drugs have been shown to improve when coordinated to a ruthenium centre. This work, thus, hypothesizes that cyclopentadienyl dicarbonyl ruthenium(II) amine complexes can be effective catalysts for the oxidation of olefins and active as antimicrobial agents.

### *1.8 Aim and objectives*

The main aim of this study was to find a procedure for the synthesis various ruthenium(II) cationic complexes, characterize them and test their catalytic and antimicrobial activities. The findings may improve the understanding of the nature of bonding and structure of the complexes and, hence, provide an insight into the possible development of homogenous oxidation catalysts based on similar or the same complexes. Furthermore, the findings from this study may ultimately inspire more research directed towards the development of similar complexes for use as antimicrobial agents against the documented drug-resistant bacteria. Thus, the following specific objectives of the study were outlined:

a) To develop a procedure for the synthesis of amine complexes of $\eta^5$-cyclopentadienyldicarbonylruthenium(II) and $\eta^5$-pentamethylcyclopentadienyldicarbonylruthenium(II)

b) To synthesize and characterize amine complexes of $\eta^5$-cyclopentadienyldicarbonylruthenium(II) and $\eta^5$-pentamethylcyclopentadienyldicarbonylruthenium(II).

c) To study the bonding and structures of nitrogen containing ruthenium complexes, compare them with the reported analogous iron complexes and provide possible explanation for any observed difference in behavior.

d) To determine the antimicrobial activities of the $\eta^5$-cyclopentadienyldicarbonylruthenium(II) amine.

e) To determine the catalytic activity of the $\eta^5$-cyclopentadienyldicarbonylruthenium(II) amine complexes

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# CHAPTER TWO

## Synthesis, characterization and crystal structure of two polymorphs of iodo-bridged ruthenium (1+)tetracarbonylbis($\eta^5$-2,4-cyclopentadien-1-yl) μ-iodidotetrafluoroborate salt

Eunice A. Nyawade, Holger B. Friedrich*, Cyprian M. M'thiruaine and Bernard Omondi
* Corresponding author

School of Chemistry and Physics, University of KwaZulu-Natal, Private Bag X54001, Durban 4000, South Africa

**Abstract**

The reaction of RpI (Rp = $(\eta^5\text{-}C_5H_5)Ru(CO)_2$) and $AgBF_4$ in two different solvents, tetrahydrofuran and dichloromethane afforded two polymorphs of the iodo-bridged cationic complex $[Rp_2I]BF_4$. Polymorph **I** precipitated out of solution as yellow broad-shaped blocks while polymorph **II** crystallized out as thin-shaped blocks. While **I** crystallized in the monoclinic P2/c space group with a = 12.0982(5) Å, b = 9.7923(4) Å, c = 15.5321(6) Å, β = 102.9880(10)°, polymorph (**II)** crystallized in the monoclinic $P2_1/c$ with a = 7.00560(10) Å, b = 14.1446(3) Å, c = 18.2226(3) Å, β = 96.2390(10)°. The IR spectra of the compound showed the presence of terminal carbonyl groups but the absence of bridging carbonyl groups. Thermal studies of the two polymorphs reveal very close melting points, 432.2 and 435.2 K for **I** and **II** respectively. The enthalpies associated with their melting are +15.1 kJ $mol^{-1}$ and +21.9 kJ $mol^{-1}$ for polymorphs **I** and **II** respectively. ESI-mass spectroscopy showed the presence of a number of statistically possible combinations of the cationic species. The two polymorphs have also been characterized using DSC, IR and NMR.

Key words: cyclopentadienylruthenium carbonyl, iodo-bridged, cationic complex, diruthenium complex salt, polymorphs, crystal structure.

## 1. Introduction

Synthesis of the halogen bridged derivatives [{(CpFe(CO)$_2$}$_2$X]Y (X = Cl, Br or I; Cp = $\eta^5$-$C_5H_5$ and Y = $BF_4$ or $PF_6$) was first reported in the mid 1960s by Fischer and Moser [1]. This was achieved by treatment of the neutral iron complex [CpFe(CO)$_2$X] with strong Lewis acids such as $AlBr_3$ and $BF_3.OEt_2$. Studies of halogenation of [CpM(CO)$_2$]$_2$ (M = Fe or Ru) [2-4] and halide abstraction in CpM(CO)$_2$X by $AgBF_4$ [5] have shown that the halogen-bridged species [{CpM(CO)$_2$X}$_2$]$BF_4$ (M = Fe or Ru; X = Cl or I) are formed as intermediate products that can be isolated under appropriate experimental conditions. Haines and co-workers [4] established that halogenation of CpRu(CO)$_2$]$_2$ in benzene or toluene forms the cation, [{CpM(CO)$_2$}$_2$X]$^+$ in the presence of large counter ions such as $PF_6^-$. In the halide abstraction from CpFe(CO)$_2$X with $AgBF_4$ [5], a silver adduct CpFe(CO)$_2$IAg is initially formed but decomposes to yield [CpFe(CO)$_2$]$^+$ and AgI. In the presence of excess CpFe(CO)$_2$I, the iodine-bridged [{CpFe(CO)$_2$}$_2$I]$BF_4$ species is formed. Similarly, a number of structures of iodine-bridged ruthenium complexes have been reported [6,7], examples of these that are similar to the structures reported here being, [($\eta$-$C_4Ph_4C$ = O)Ru(CO)$_2$]$_2$I, [6] and the cationic complex salt, [Cp*Ru(CO)$_2$]$_2$I]$^+$[B{Ph($CF_6$)$_2$}$_4$]$^-$ (Cp* = $\eta^5$-$C_5Me_5$) [7]. We hereby report the synthesis and structural characterization of two polymorphs of [Rp$_2$I]$BF_4$, both crystallizing in the monoclinic system in P2/c (**I**) and P2$_1$/c (**II**) space groups. The two polymorphs have also been characterized thermally by DSC and also by NMR, IR and mass spectrometry.

## 2. Experimental

### *2.1 General*

All reactions were carried out under inert atmosphere using standard Schlenk line techniques. Nitrogen gas (Afrox) was dried over phosphorus(V) oxide. Reagent grade THF (Merck) and $Et_2O$ (Merck) were distilled from sodium/benzophenone and stored over molecular sieves; $CH_2Cl_2$ (Merck) was distilled from phosphorous(V) oxide. Silver tetrafluoroborate (Alfa Aesar), Ruthenium trichloride hydrate (DLD), dicyclopentadiene (Aldrich), carbon monoxide (Afrox) and iodine (Unilab) were used as supplied. Melting points were recorded on an Ernst Leitz Wetzlar hot-stage microscope and are uncorrected. Elemental analyses were performed on a LECO CHNS-932 elemental analyzer. Infrared spectra were recorded using an FTIR PerkinElmer Spectrum 100 spectrophotometer between 4000 and 400 cm$^{-1}$, in dichloromethane. Mass spectra were recorded on an Agilent 1100 series LC/MSD trap with electrospray ionization (ESI) source and quadrupole ion trap mass analyzer by direct infusion and ESI

operated in the positive mode. Acetonitrile (100%) was used as mobile phase and 10 μL of the sample injected at 0.3 ml/min flow rate. NMR spectra were recorded on Bruker topspin 400 and 600 MHz spectrometers. The deuterated solvents $CDCl_3$ (Aldrich, 99.8%) and acetone-$d_6$ (Aldrich, 99.5%), were used as purchased. Solutions for NMR spectroscopy were prepared under nitrogen using nitrogen-saturated solvents. DSC curve was recorded on a SDT Q600 V20.9 Build 20 instrument using nitrogen at a flow rate of 10/min. The precursors $Ru_3(CO)_{12}$ [8], $[CpRu(CO)_2]_2$ [9], $CpRu(CO)_2I$ [4], and $[Cp(CO)_2Ru]BF_4$ [10] were prepared by the literature methods.

### *2.2 Preparation of polymorph I of $[Rp_2I]BF_4$*

A mixture of RpI (0.58 mmol) and a slight excess of silver tetrafluroborate were added into an aluminium foil-wrapped, dry Schlenk tube and dried under reduced pressure for 1hr to remove any water absorbed by $AgBF_4$ during transfer. Dry, deoxygenated THF (30 mL) was added and the mixture stirred at 0 °C for 3 h. The solvent was evaporated at reduced pressure leaving a dark-gray solid. The residue was extracted with two 10 mL portions of $CH_2Cl_2$. The mixture was filtered by use of a canula. An orange coloured filtrate was obtained. The filtrate was concentrated and dry diethyl ether was slowly added to the concentrated filtrate to precipitate out the product. The mixture was kept at −20 °C for 30 min and a pale yellow solid was formed. It was washed with diethyl ether and dried under reduced pressure. The solid was characterized by NMR spectroscopy and found to be a mixture of products. Analysis: $^1$H NMR (600 MHz, $C_3D_6O$): δ 6.39 (s, 5H, Cp), δ 6.00 (s, Cp), δ 5.90 (s, 5H, Cp) and δ 5.73 (s, 5H, Cp). $^{13}$C NMR (600 MHz, $C_3D_6O$): δ 92.49 (Cp), δ 89.75 (Cp), δ 88.9 (Cp), δ 88.42 (Cp), δ 196.55 (CO) and δ 189.60 (CO). The product was then dissolved in 2 mL of $CH_2Cl_2$ in a vial. Dry, deoxygenated diethyether (4 mL) was slowly added to form a layer on the solution. The vial was wrapped with an aluminium foil and left for 24 h. Yellow needle shaped crystals were formed. Analysis: Calc. For $C_{14}H_{10}IO_4BF_4$: C, 25.55%; H, 1.53% and found for $C_{14}H_{10}IO_4BF_4$: C, 24.72%; H, 1.84%. $^1$H NMR (400 MHz, $CDCl_3$): δ 5.72 (s, 5H, Cp). $^{13}$C NMR (400 MHz, $CDCl_3$): δ 88.40 (Cp), 194.70 (CO). FTIR in $CH_2Cl_2$ one broad ν(CO) stretch split at tip (2068 and 2058) and 2017 $cm^{-1}$; one ν(Cp) peak split at the tip to give 3056 and 3052 $cm^{-1}$ . Melting point is 432.2 K. Es-ms (positive mode) m/z: 572.8 { 15.50% $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4I]^+$}, exact mass calc. for $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4I]^+$ 572.8; 543.8 {13.37% $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_3I]^+$exact mass calc. for $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_3I]^+$ 543.8; 515.8 {35.37% $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_2I]^+$}, exact mass calc. for $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_2I]^+$ 515.8; 488.8 {35.76% $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)I]^+$, exact mass calc. for $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)I]^+$ 488.8.

### *2.3 Preparation of polymorph II of $[Rp_2I]BF_4$*

Polymorph **II** of $[Rp_2I]BF_4$ was obtained when a mixture of RpI (0.454 g; 1.299 mmol) and an equimolar amount of silver tetrafluroborate (0.253 g; 1.299 mmol) were added into an aluminium foil-wrapped, dry Schlenk tube and dried under reduced pressure for 1 h to remove any water absorbed by $AgBF_4$ during transfer. Dry, deoxygenated (30 mL) $CH_2Cl_2$ was added and the mixture stirred for 2 h after which it was filtered by canula and excess solvent removed under reduced pressure. A dark green coloured filtrate was obtained. The filtrate was concentrated under reduced pressure. Dry diethyl ether was slowly added to the filtrate. An orange precipitate was formed, leaving a dark-green mother liquor. The orange precipitate was washed with diethyl ether and characterized. It was found to melt at 435.2 K. Elemental analysis, IR spectroscopy, NMR spectroscopy and mass spectrometry results for polymorph **II** are similar to those observed and recorded for polymorph **I**.

### *2.4 X-ray crystal structure determination of $[\{(Cp(CO)_2Ru)_2\}I]BF_4$*

Crystals of $[\{(Cp(CO)_2Ru)_2\}I]BF_4$ suitable for single crystal X-ray diffraction studies were grown by the liquid diffusion method. Solutions of the compounds in dry $CH_2Cl_2$ were layered with a fourfold of excess diethyl ether and allowed to stand undisturbed in the dark at room temperature for 24 h. Crystals of the two polymorphs were selected and glued onto the tip of glass fibres. The crystals were then mounted in a stream of cold nitrogen at 100(1) K and centred in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Smart APEXII diffractometer with Mo Kα radiation (λ = 0.71073 Å). The diffractometer to crystal distance was set at 4.00 cm. The initial cell matrix was obtained from three series of scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range about with the exposure time of 10 s per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite [11]. The final cell constants were calculated from a set of 6460 strong reflections from the actual data collection. Data collection method involved ω scans of width 0.5°. Data reduction was carried using the program SAINT+ [11]. The structure was solved by direct methods using SHELXS [12] and refined [11]. All structures were checked for solvent-accessible cavities using PLATON [13] and the graphics were performed with the DIAMOND [14] visual crystal structure information system software. Non-H atoms were first refined isotropically and then by anisotropic refinement with

full-matrix least-squares calculations based on $F^2$ using SHELXS. All H atoms were positioned geometrically and allowed to ride on their respective parent atoms. The carboxyl H atoms were located from the difference map and allowed to ride on their parent atoms. All H atoms were refined isotropically. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [11]. Crystal data and structure refinement information for polymorph **I** and **II** are summarized in Table 1.

**Table 1:** Crystal data and structure refinement for polymorphs I and II

| | Polymorph I | Polymorph II |
|---|---|---|
| Empirical formula | $C_{14}$ $H_{10}$ B $F_4$ I $O_4$ $Ru_2$ | $C_{14}$ $H_{10}$ B $F_4$ I $O_4$ $Ru_2$ |
| Formula weight | 658.07 | 658.07 |
| Temperature | 173(2) K | 173(2) K |
| Wavelength | 0.71073 Å | 0.71073 Å |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P2/c | P21/c |
| Unit cell dimensions (Å / °) | a = 12.0982(5)<br>b = 9.7923(4) β= 102.9880(10)<br>c = 15.5321(6) | a = 7.00560(10)<br>b = 14.1446(3) β= 96.2390(10)<br>c = 18.2226(3) |
| Volume | 1793.00(13) $Å^3$ | 1795.01(5) $Å^3$ |
| Z | 4 | 4 |
| Density (calculated) | 2.438 $Mg/m^3$ | 2.435 $Mg/m^3$ |
| Absorption coefficient | 3.462 $mm^{-1}$ | 3.458 $mm^{-1}$ |
| F(000) | 1232 | 1232 |
| Crystal size | 0.43 x 0.34 x 0.16 $mm^3$ | 0.42 x 0.16 x 0.11 $mm^3$ |
| Theta range for data collection | 1.73 to 28.45°. | 1.83 to 28.32°. |
| Index ranges | -16≤h≤15, -13≤k≤11,<br>-20≤l≤20 | -8≤h≤9, -18≤k≤18,<br>-24≤l≤22 |
| Reflections collected | 46542 | 42242 |
| Independent reflections | 4492 [R(int) = 0.0247] | 4471 [R(int) = 0.0244] |
| Completeness to theta = 28.45° | 99.2 % | 99.8 % |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max. and min. transmission | 0.6858 and 0.4069 | 0.7022 and 0.3245 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4492 / 0 / 236 | 4471 / 28 / 235 |
| Goodness-of-fit on $F^2$ | 1.201 | 1.111 |
| Final R indices [I>2sigma(I)] | R1 = 0.0141, wR2 = 0.0378 | R1 = 0.0127, wR2 = 0.0322 |
| R indices (all data) | R1 = 0.0149, wR2 = 0.0385 | R1 = 0.0135, wR2 = 0.0326 |
| Largest diff. peak and hole | 0.408 and -0.837 $e.Å^{-3}$ | 0.462 and -0.621 $e.Å^{-3}$ |

## 3. Results and discussion

### *3.1 Synthesis*

The reaction between RpI and $AgBF_4$ in THF yields the iodide-bridged complex salt, $[Rp_2I]BF_4$ **(I)** as a major product and the expected THF salt, $[Rp(THF)]BF_4$, as a minor product. Similar reactions on the Fe analogue, $CpFe(CO)_2I$ and $AgBF_4$ in THF preferentially result in $[(CpFe(CO)_2(THF)]BF_4$ [10] types of complexes. On carrying out the same reaction of RpI and $AgBF_4$ in dichloromethane as the solvent, a different polymorph of $[Rp_2I]BF_4$ **(II)** is formed. The NMR spectra of the two polymorphs are the same, but their melting points differ slightly, 432.2 and 435.2 K for **I** and **II** respectively. Polymorph **I** crystallize as yellow broad blocks, while **II** crystallizes also as yellow but thinner blocks.

### *3.2 IR and NMR spectroscopic studies*

Polymorphs **I** and **II** have similar IR spectral properties. The IR spectra of the two polymorphs recorded in dichloromethane gave two characteristic ν(CO) absorption bands, at 2069 and 2014 $cm^{-1}$, suggesting terminally bound CO ligands. These IR signals are in agreement with the literature values for $[Rp_2I]BF_4$ [4]. A band corresponding to the cyclopentadienyl anion stretching was also observed at 3122 $cm^{-1}$. In the IR spectrum of a crude sample of polymorph **I** in dichloromethane, additional weak bands at 2945 $cm^{-1}$ and 2874 $cm^{-1}$ associated with C−H stretching in THF were observed, an indication of the minor product, $[Rp(THF)]BF_4$, from the reaction. The crystals gave strong νCO stretching frequencies at 2068 $cm^{-1}$, and 2016 $cm^{-1}$. The NMR spectrum of the crude product **I** in acetone-d at 25 °C also confirmed the formation of the minor product, as extra resonance peaks associated with the Cp ring protons of the major and minor products, were observed at 6.37, 6.00, 5.90 and 5.73 ppm. These peaks may be associated with protons of $\eta^5$-$C_5H_5$ of $[Rp\{OC(CH_3)_2\}]BF_4$, $[Rp_2I]BF_4$, $[Rp\{H_2O\}]BF_4$, and RpI respectively. The $^{13}C$ NMR spectrum also gave four signals associated with cyclopentadienyl rings at 92.49 ppm, 89.75 ppm, 88.90 ppm and 88.42 ppm. $^1H$ NMR spectra were obtained in acetone–d for authentic samples of $[Rp_2I]BF_4$ (6.00 ppm) and RpI (5.72 ppm) prepared according to literature methods.

$$[Rp(THF)BF_4 + H_2O \longrightarrow [Rp(H_2O)]BF_4 + THF \quad (1)$$

The aqua complex, $[CpFe(CO)_2(H_2O)]BF_4$, is readily formed when even adventitious water is available around the THF complex $[CpFe(CO)_2(THF)]BF_4$ [1]. It is therefore assumed, based on the extra resonance peaks in the $^1H$ and $^{13}C$ NMR spectra, that a similar reaction may have taken place in the NMR tube, hence the presence of $[Rp(H_2O)]BF_4$ due to the presence of adventitious water in the wet deuterated acetone as shown in Eq. (1).

$$[Rp(THF)]BF_4 + (CH_3)_2CO \longrightarrow [RpOC(CH_3)_2]BF_4 + THF \quad (2)$$

Similarly, the acetone complex, $[Rp\{OC(CH_3)_2\}]BF_4$ is probably formed by rapid displacement of THF by deuterated acetone molecules (Eq. (2)). It has been reported that at high temperatures the acetone complex forms [10] and since the NMR samples were not freshly made, there is a chance that it forms. The reaction between $AgBF_4$ and an equimolar quantity or a slight excess of RpI gives a product $[(Rp)_2I]BF_4$ and not the expected final product $[Rp]BF_4$. The same happens for the formation of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2I]^+$ from the halide abstraction reaction of $CpFe(CO)_2I$ by $AgBF_4$ [5] as one of the intermediates. The main product when 2 equivalents of $CpFe(CO)_2I$ are reacted with 1 equivalent of $AgBF_4$ is $[\{CpFe(CO)_2\}_2I]BF_4$. The complex $[(Rp)_2I]BF_4$ is formed according to equations 3 and 4 [15].

$$RpI + AgBF_4 \longrightarrow [Rp]BF_4 + AgI \quad (3)$$

$$[Rp]BF_4 + RpI \longrightarrow [Rp_2I]BF_4 \quad (4)$$

In the $^{13}C$ NMR spectrum in acetone-d, two CO signals are observed at 196.55 ppm and 189.60 ppm. The signal at 189.60 ppm is assignable to the carbon on the CO group of **I**. The $^1H$ and $^{13}C$ NMR spectra of **II** were obtained using $CDCl_3$ and the resonance signals observed at 5.73 ppm, 5.60 ppm and 5.53 ppm correspond with the same observed for the cyclopentadienyl ring in $[Rp(H_2O)]^+$ (5.62 ppm), $\{[(Rp)_2]I\}^+$ (5.74 ppm) and RpI (5.45 ppm). The proton resonance signal observed in the experiment done in acetone-d which was assigned to the acetone compound was absent when $CDCl_3$ is used as the solvent. The $^{13}C$ NMR spectrum gave 3 carbon resonance signals for the Cp carbons at 88.37 ppm, 86.65 ppm and 86.59 ppm. A carbonyl resonance signal was observed at 194.70 ppm.

### *3.3 Electro spray mass spectrometry*

The identification of the cationic nature of various species was done by analysis of the isotopic abundance for ruthenium ($^{96}$Ru 5.5%, $^{98}$Ru 1.9%, $^{99}$Ru 12.8%, $^{100}$Ru 12.6%, $^{101}$Ru 17.1%, $^{102}$Ru 31.6% and $^{104}$Ru 18.6%) and for their statistical combinations ($^{96}$Ru and $^{98}$Ru, $^{98}$Ru and $^{99}$Ru, $^{99}$Ru and $^{100}$Ru, $^{100}$Ru and $^{101}$Ru, $^{101}$Ru and $^{102}$Ru, and $^{102}$Ru and $^{104}$Ru) in the cationic species, $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4I]^+$ (see Fig 1). The electro spray mass spectrum shows that the most abundant fragments are $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_2I]^+$ and $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)\ I]^+$ with greatest peaks intensities at $3.65 \times 10^6$ (m/e = 515.8) and $3.69 \times 10^6$ (m/e = 488.8), whereas the least abundant fragment is $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_3I]^+$ with its greatest peak intensity at $1.38 \times 10^6$ (m/e = 543.8). Table 2 shows molecular masses of some of the cationic complex fragments detected by the mass spectrometer.

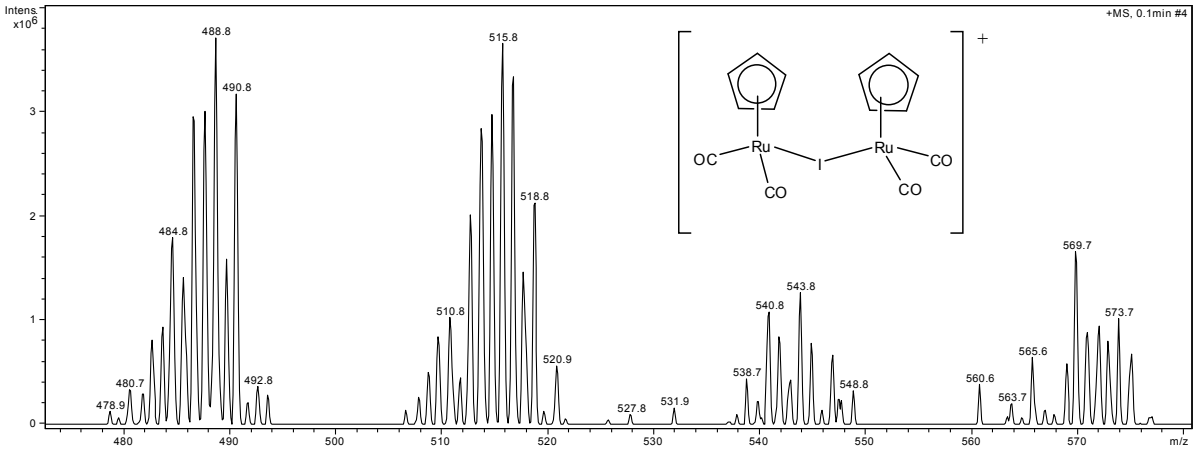


**Figure 1:** Electro spray mass spectrum of the iodo-bridged complex

**Table 2:** Molecular masses of the cationic complex $[CpRu_2(CO)_4]\ I^+$ and subsequent cationic fragments containing different ruthenium isotopes

| **Ru isotopes in molecule** | **Molecular cationic masses** | | | |
|---|---|---|---|---|
| | **$[Cp_2Ru_2(CO)_4]^+$** | **$[Cp_2Ru_2(CO)_3]^+$** | **$[Cp_2Ru_2(CO)_2]^+$** | **$[Cp_2Ru_2(CO)]^+$** |
| $^{96}$Ru × 2 | 560.8 | 532.8 | 504.8 | 476.8 |
| $^{96}$Ru and $^{98}$Ru | 562.8 | 534.8 | 506.8 | 478.8 |
| $^{98}$Ru × 2 | 564.8 | 536.8 | 508.8 | 480.8 |
| $^{98}$Ru and $^{99}$Ru | 565.8 | 537.8 | 509.8 | 481.8 |
| $^{99}$Ru × 2 | 566.8 | 538.8 | 510.8 | 482.8 |
| $^{99}$Ru and $^{100}$Ru | 567.8 | 539.8 | 511.8 | 483.8 |

| Ru isotopes in molecule | Molecular cationic masses | | | |
|---|---|---|---|---|
| | $[Cp_2Ru_2(CO)_4]^+$ | $[Cp_2Ru_2(CO)_3]^+$ | $[Cp_2Ru_2(CO)_2]^+$ | $[Cp_2Ru_2(CO)]^+$ |
| $^{100}Ru \times 2$ | 568.8 | 540.8 | 512.8 | 484.8 |
| $^{101}Ru$ and $^{100}Ru$ | 569.8 | 541.8 | 513.8 | 485.5 |
| $^{101}Ru \times 2$ | 570.8 | 542.8 | 514.8 | 486.8 |
| $^{101}Ru$ and $^{102}Ru$ | 571.8 | 543.8 | 515.8 | 487.8 |
| $^{102}Ru \times 2$ | 572.8 | 544.8 | 516.8 | 488.8 |
| $^{102}Ru$ and $^{104}Ru$ | 574.8 | 546.8 | 518.8 | 490.8 |
| $^{104}Ru \times 2$ | 576.8 | 548.8 | 520.8 | 492.8 |

Species with the different isotopes of ruthenium all readily release the counter anion $BF_4^-$ leaving the cationic complex, $[(Rp)_2I]^+$, whose molecular ions m/e range from 560.6 to 576.8, with the most abundant complex peak at 569.7. The peak at 569.7 corresponds to the mass of the cationic complex molecule consisting of $^{100}Ru$ and $^{101}Ru$ isotopes whose atomic masses are 99.91 and 100.91 respectively. Subsequent fragments, $[Cp_2Ru_2(CO)_3I]^+$, $[Cp_2Ru_2(CO)_2I]^+$ and $[Cp_2Ru_2(CO)I]^+$, whose molecular ions m/e range from 538.7 to 548.8, 508.8 to 520.8, and 480.7 to 492.8 respectively, show the sequential loss of carbonyl groups. This is clear proof that the yellow crystals are of the iodide-bridged complex $[Cp_2Ru_2(CO)_4I]^+BF_4^-$. The Cp anion remained coordinated to the ruthenium metal in all the fragments. This shows that the carbonyl groups are more weakly coordinated than the Cp anion and hence more readily lost to give the various cationic fragments. The presence of two ruthenium atoms and an iodine atom in all the fragments shows that the Ru−I bond was also not affected in the fragmentation process.

### *3.4 Thermal analysis*

$[Rp_2I]^+BF_4^-$ has two polymorphic forms, with similar crystal shapes both being blocks but with slightly different shades of orange. Figure 2 shows DSC traces of the two polymorphs during the first heating cycle. The DSC experiments were done between the temperatures of 298 K and 1173.15 K. In the traces, data has been reported for the range between 360 and 610 K as nothing meaningful was observed outside of this range. The traces showed endotherms at 432.2 and 435.2 K for polymorphs **I** and **II** respectively, corresponding to their respective melting points. Two other endotherms are observed at 562.83 and 600.71 K corresponding to their respective decomposition temperatures. The area under the curve at the melting point of polymorph **I** was determined and found to be 26.42J/g. The enthalpies associated with the melting point endotherms are +15.1 kJ/mol and +21.9 kJ/mol for polymorphs **I** and **II** respectively. The

difference in the two energies could be due to the difference in packing and intermolecular interactions.

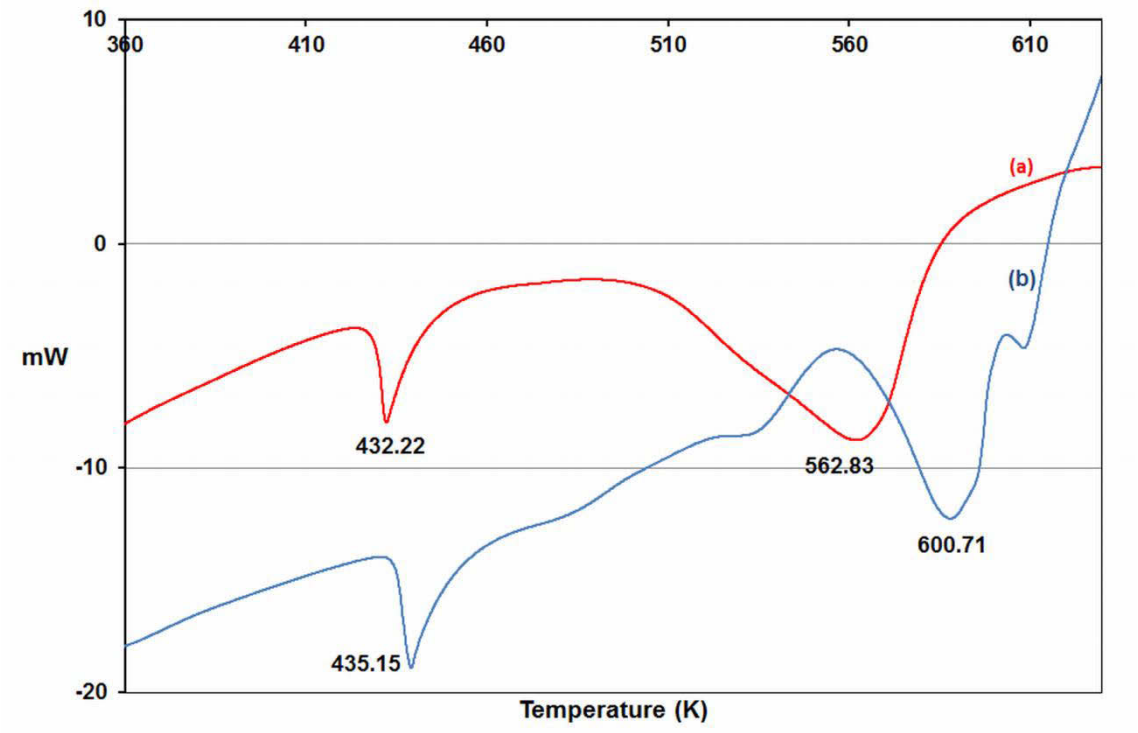


**Figure 2:** An overlay of the DSC traces for (a), polymorph (**I**) and (b), polymorph (**II**)

### *3.5 Molecular and crystal structure analysis*

The two polymorphs of Ruthenium(I)tetracarbonylbis($\eta^5$-cyclopentadienyl)-μ-iodido tetrafluoroborate have different molecular geometries but crystallize to form dinuclear ruthenium cationic complex salts of tetrafluoroborate (Figures 3 and 4). Both polymorphs crystallized into yellow (**I**) and pale yellow (**II**) blocks in a monoclinic crystal system, but with different space groups; P2/c and $P2_1/c$.

The combined electron count is 35 with a mean oxidation state of +2 on each ruthenium in each polymorph. In both polymorphs, the Ru atom is coordinated in a pseudo-octahedral three-legged piano-stool fashion; with the $\eta^5$-coordinated cyclopentadienyl ligand occupying apical positions while the two carbonyl groups and the bridging iodide anion occupying the basal positions. Both polymorphs have one molecule of the dinuclear ruthenium cation in the asymmetric unit. Whereas the tetrafluoroborate anion is split into two halves in polymorph I, specially positioned at $\left(\frac{1}{2}, 1, \frac{4}{3}\right)$and at$\left(0, \frac{1}{2}, \frac{3}{4}\right)$, in polymorph II, the whole anion is in one position in the asymmetric

unit. Only one iodide bridged ruthenium compound similar to polymorphs I and II can be found in literature [10] and that was found to be a neutral compound.

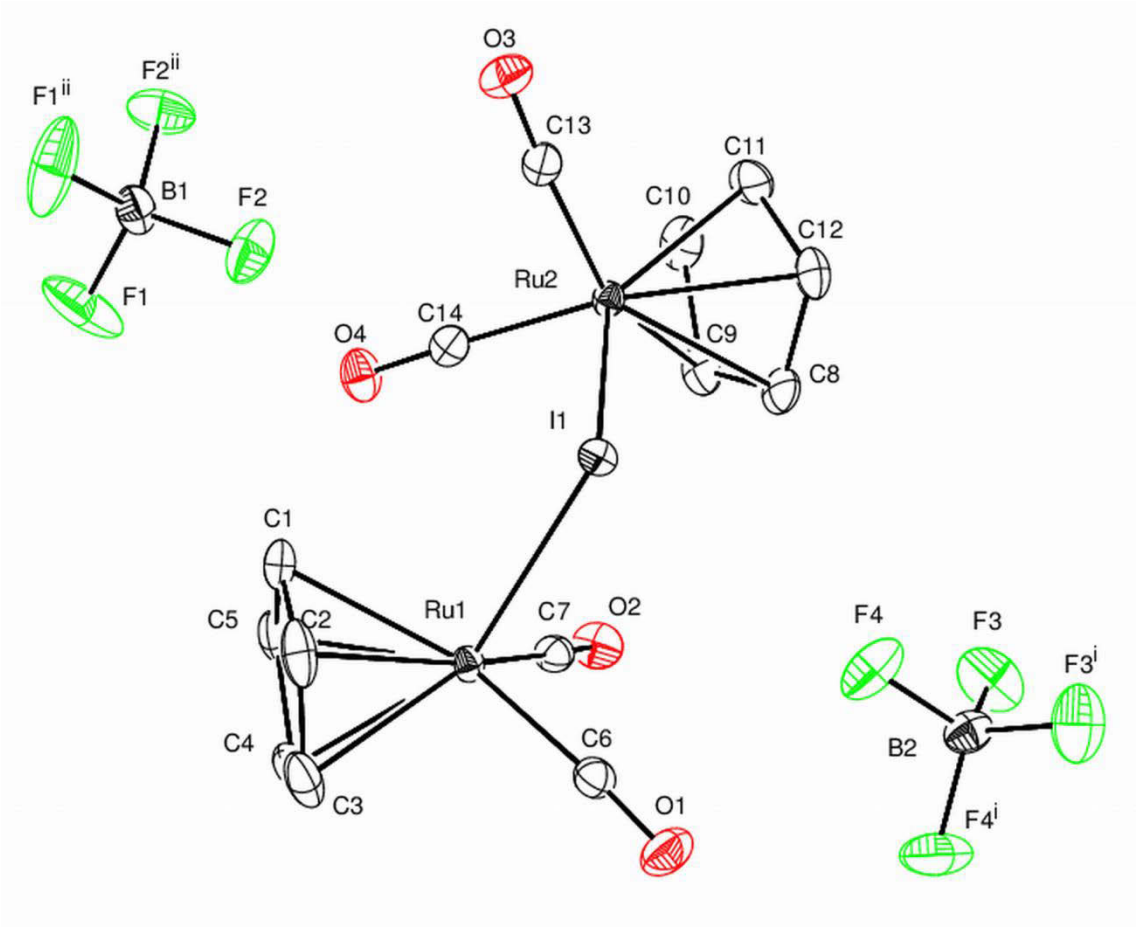


**Figure 3:** The molecular structure of polymorph **I** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are not shown

However, polymorph **I** has similar cell parameters as μ-iodo-bis($\eta^5$-cyclopentadienyl-dicarbonyl-iron)tetrafluoroborate [4] whose glide is along the crystallographic a axis ($P2_a$) as opposed to the c axis in **I**. In both polymorphs, the $CpRu(CO)_2$ are staggered, the degree of staggering being larger in **I** with the dihedral angle Cg–Ru···Ru–Cg of 148.88(7)° and only 46.90(9) in **II**. In **I**, the Ru–I–Ru bond angle is 106.91 (5)° while in **II** the same angle is 111.98(5)°, that of **II** being closer to the Fe-I-Fe in μ-iodo-bis($\eta^5$-cyclopentadienyl-dicarbonyl-iron)tetrafluoroborate [4] (110.8(1)°). These are comparable to values obtained for the related complex $\{[Cp^*Ru(CO)_2]_2I\}^+$ where the angle is 113° [7]. The orientations of the two Cp rings in both polymorphs are different and in **I** the torsional angles (Table 3) Cg–Ru–I–Ru are closer to being orthogonal [94.36(8) and 98.59(8)°] as compared to those of polymorph **II** [76.35(8) and

131.17(6)°]. These torsion angles are closer in **II** to those of μ-iodo-bis($\eta^5$-cyclopentadienyl-dicarbonyl-iron)tetrafluoroborate [4]. However, the Cg–Ru–I bond angles are comparable in both polymorphs and are 119.70(2) and 123.34(3) in **I** and 121.18(3) and 122.15(3)° in **II**.

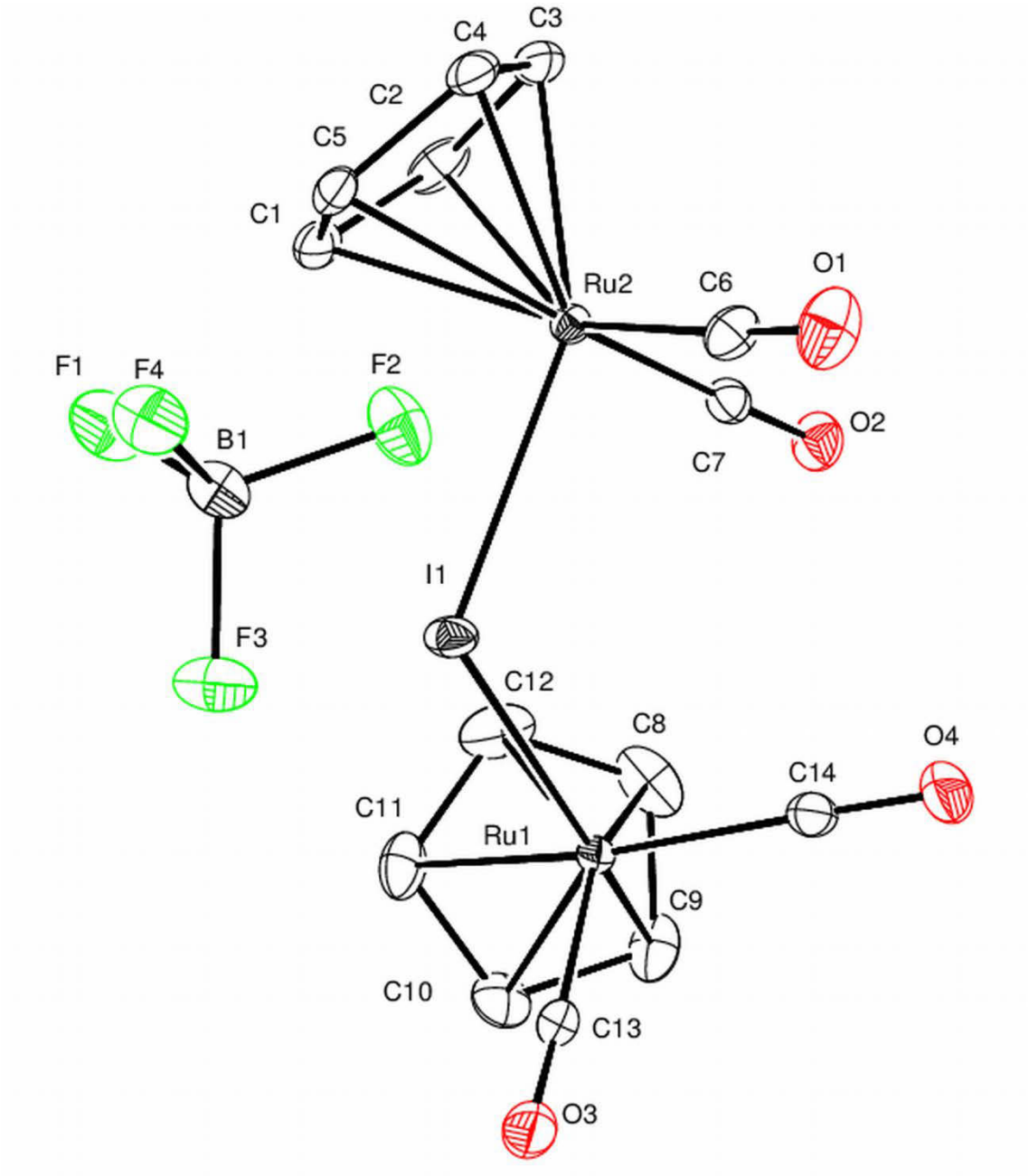


**Figure 4:** The molecular structure of polymorph **II** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are not shown

**Table 3:** Selected bond distances (Å) and angles ( °)

| | **I** | **II** | **Ref 4b** |
|---|---|---|---|
| Ru−I | 2.68658(18) | 2.69093(15) | 2.666 |
| Ru−I | 2.69787(18) | 2.68768(15) | 2.685 |
| Ru−I−Ru | 106.91(5) | 111.98(5) | 113.0 |
| Cg−Ru−I | 119.7(2) | 121.18(3) | 122.1 |
| Cg−Ru−I | 123.34(3) | 122.15(3) | 124.5 |
| Cg−Ru···Ru−Cg | 148.88(7) | 46.90(9) | 50.71 |
| Cg−Ru−I−Ru | 94.36(8) | 76.35(8) | 118.8 |
| Cg−Ru−I−Ru | 98.59(8) | 131.17(8) | 159.9 |

Cg is the centroid for C1-C5 of the Cp ring

The Ru−I bond lengths are 2.68658(18) Å and 2.69707(18) Å respectively for polymorph **I** and 2.69093(15) Å and 2.68768(15) Å for polymorph **II** (Table 3). These bonds are comparable to those observed for the related compound, $[\{(\eta^5\text{-}C_5Me_5)Ru(CO)_2\}_2I]^+$ [7] (Ru−I1 = 2.666(3) Å; Ru2−I1 = 2.685(3) Å). The same bond distances are slightly longer in $[\{(\eta^5\text{-}OC_5Ph_4)Ru(CO)_2\}_2I]$ (Ru1−I = 2.727(1) Å ; I−Ru2 = 2.714(1) Å) [6].

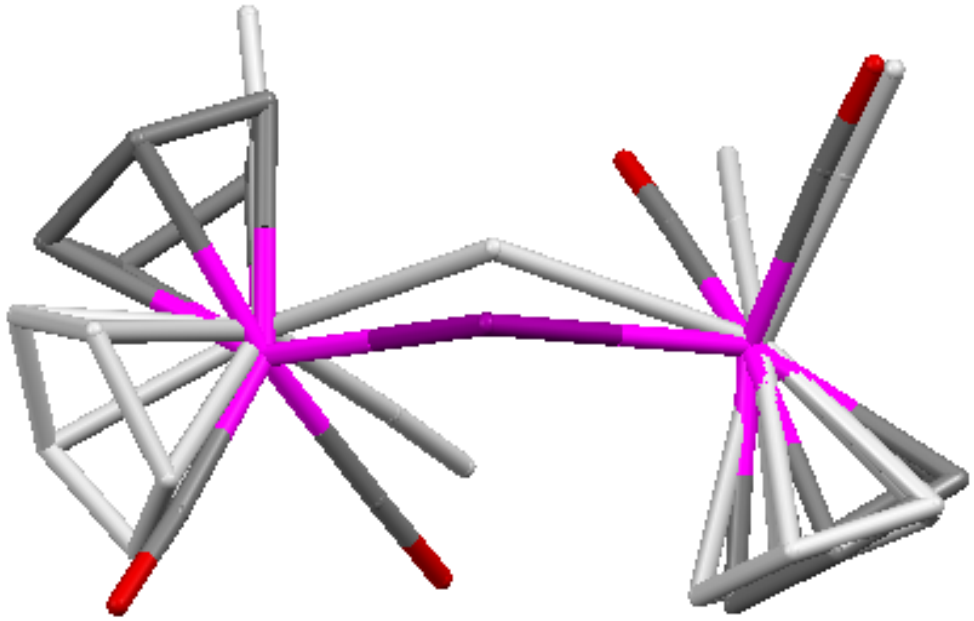

**Figure 5:** The root mean square deviation overlay picture of the two cations

Figure 5 shows the root mean square deviation overlay of the two cations. The root mean square deviation for the two cations is 1.6169. This value is large due to the difference in the orientation of the Cp−Ru moieties. The densities of the two polymorphs are very similar. Polymorph **I** is only denser than polymorph **II** by 0.003 mg/m$^3$, a probable indication that the stabilities of the two polymorphs are similar. Furthermore the packing indices as calculated by platon [13] for both polymorphs reveal no voids in the structures and are 73.4% and 73.5% for **I** and **II** respectively, even though the packing patterns are vastly different (see Figs. 6 and 7).

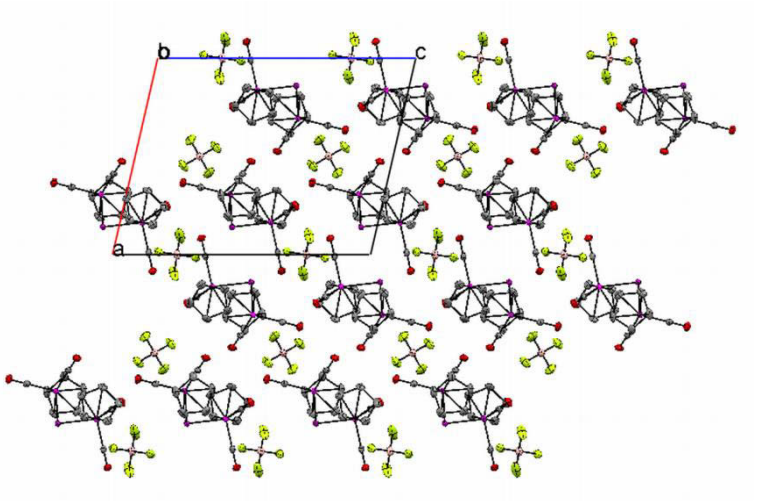


**Figure 6:** Packing diagram for polymorph **I** viewed along the b-axis with hydrogen atoms omitted for clarity

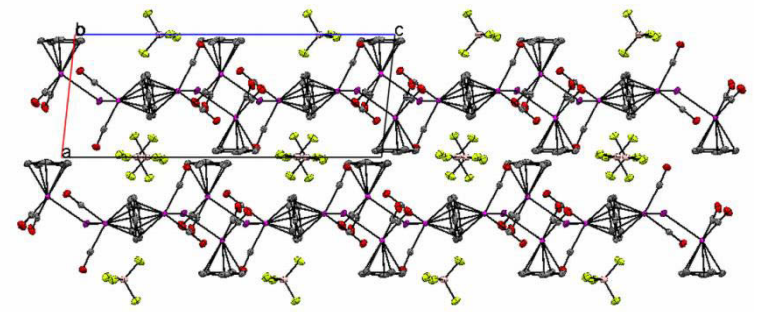


**Figure 7:** Packing diagram for polymorph **II** viewed along the b-axis

In the crystal structures of the two polymorphs, π···π (**I**) and C−H···F intermolecular interactions (**I** and **II**) play a role in the packing (Table 4). In polymorph **I**, the cationic molecules are connected in a head-to-tail fashion through π···π intermolecular interactions with

a Cg···Cg distance of 3.8520(12) Å [symmetry code; $x$, 1 + y, z] resulting in chains that run along the crystallographic b axis (Fig. 6). In between the chains are the tetrafluoroborate anions which, through two C−H···F intermolecular interactions, link up the chains to form sheets along the diagonal of the ac face (Fig. 8). In the crystal of polymorph **II** the anion is involved in three C−H···F intermolecular interactions through three of its fluorine atoms. F3 and F4 link two cations related by a c-glide through C1−H1···F4 and C10−H10···F3 intermolecular interactions. These interactions are further stabilized by C4-H4…F3 intermolecular interactions and a C5−H5···F1 intramolecular interaction (Fig. 9).

**Table 4:** C-H…F intermolecular interactions in polymorphs I and II (Å / °)

| **C−H···X** | **D−H** | **H···A** | **D···A** | **D−H···A** | **Symmetry codes** |
|---|---|---|---|---|---|
| **Polymorph I** | | | | | |
| C1−H1···F2 | 0.98 | 2.31 | 3.286(2) | 171 | Intramolecular |
| C2−H2···F2 | 0.98 | 2.23 | 3.167(2) | 160 | -x, 1-y, 1-z |
| C8−H8···F4 | 0.98 | 2.51 | 3.319(2) | 175 | X, -y, ½+z |
| **Polymorph II** | | | | | |
| C1−H1···F4 | 0.98 | 2.37 | 3.3388(19) | 168 | 1+x, y, z |
| C4−H4···F3 | 0.98 | 2.34 | 3.2711(18) | 159 | -x, -½+y, ½-z |
| C5−H5···F1 | 0.98 | 2.38 | 3.2989(18) | 155 | Intramolecular |
| C10−H10···F3 | 0.98 | 2.34 | 3.291(2) | 165 | 1-x, 1-y, 1-z |

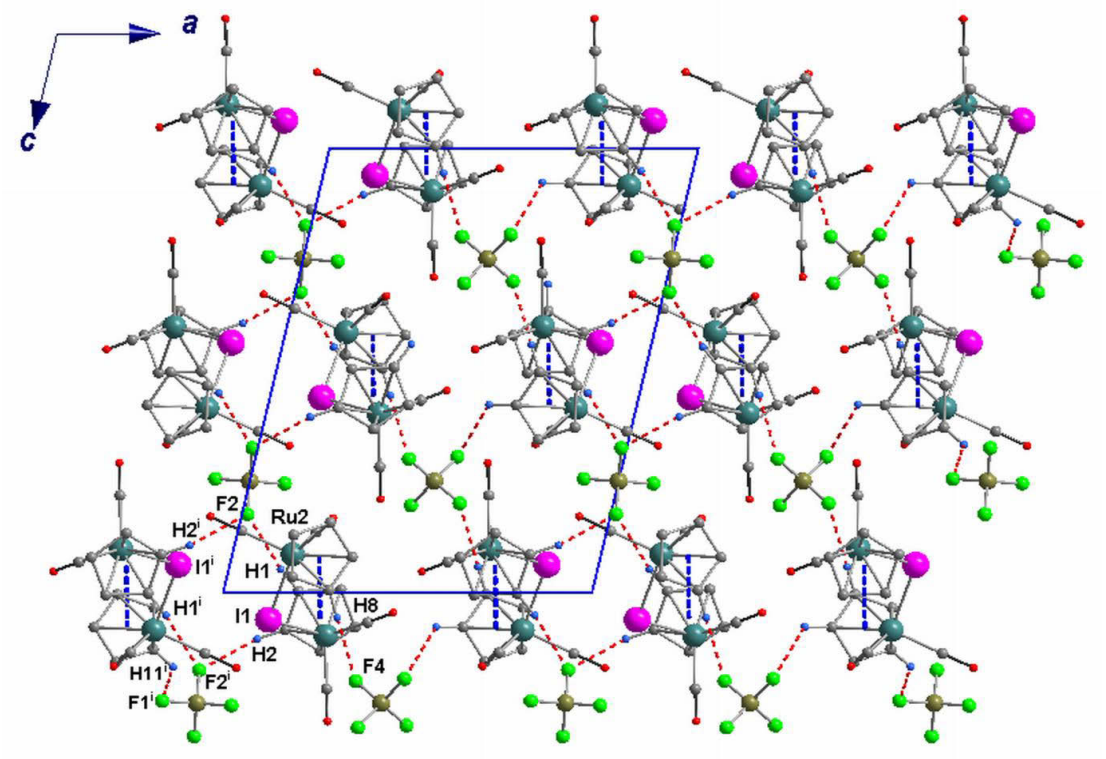


**Figure 8:** Hydrogen bonding diagram for polymorph **I**. π…π interactions are shown in bold blue dashed lines while C-H…F interactions are shown in thin red dashed lines as viewed down the crystallographic b axis. Symmetry operator: i = -x, -y, 2-z

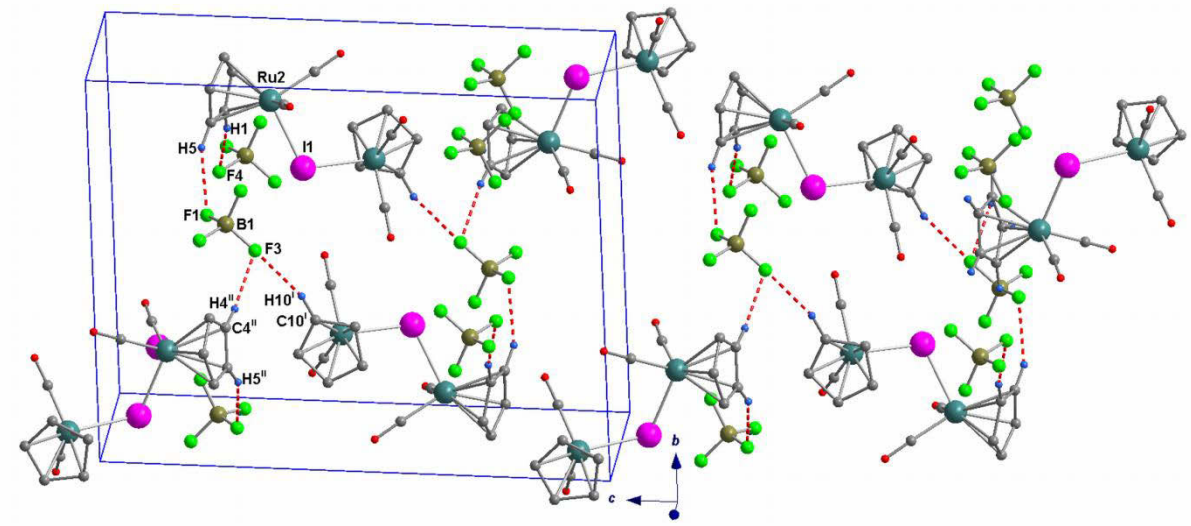


**Figure 9:** A perspective of polymorph **II** showing C-H…F intermolecular interactions in red dashed lines. Symmetry operators: I = 1-x, 1-y, 1-z; II = 2-x, -½+y, 3/2-z

## *4. Conclusion*

The $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4I]^+$ cation consists of an iodide bridge, Rp−I−Rp, and exists in two polymorphic forms with similar spectral properties. The crystal structures of the polymorphs also confirm that the CO groups are terminal and not bridging. They have different crystal packing leading to different melting points and hence enthalpies of fusion. The formation of the polymorphs seems to be dependent on the solvent used during preparation. The complex consist of $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4I]^+$ cationic molecules. The CO groups in the cation are readily lost as shown by the fragmentation patterns in the mass spectra. This suggests that the CO groups are not as strongly bonded to the metal cations as are the Cp and I anions.

**Acknowledgements**

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**Supplementary material**

CCDC 934493 and 934494 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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# CHAPTER THREE

## Synthesis, characterization and crystal structures of new water-soluble 1-alkanamine-dicarbonyl($\eta^5$-cyclopentadienyl)ruthenium(II) tetrafluoroborate complex salts

Eunice A. Nyawade, Holger B. Friedrich* and Bernard Omondi

* Corresponding author

School of Chemistry and Physics, University of KwaZulu-Natal, Private Bag X54001, Durban 4000, South Africa

**Abstract**

New water-soluble 1-alkanaminedicarbonyl($\eta^5$-cyclopentadienyl)ruthenium(II) tetrafluoroborate complex salts, $[CpRu(CO)_2NH_2R]^+BF_4^-$ (Cp = $\eta^5$-$C_5H_5$ (R = $CH_3$ **1**, $C_2H_5$ **2**, $C_3H_7$ **3**, $C_4H_9$ **4,** $C_5H_{11}$ **5** and $C_6H_{13}$ **6**), were synthesized by the reaction of the organometallic Lewis acid, $[CpRu(CO)_2]^+BF_4$, with slight excesses of 1-alkanamines, $RNH_2$, in dry methylene chloride at room temperature and pressure. These compounds are reported for the first time and have been fully characterized by IR, electrospray ionization mass spectrometry, $^1H$ and $^{13}C$ NMR spectroscopy, and elemental analysis. Spectral data show that the n-alkanamines are σ-bonded to the metal centre via the nitrogen atom. Complexes **2** to **5** were characterized by single crystal X-ray diffraction and all four cationic species feature a "pseudo-octahedral three-legged piano stool" structure in which the ruthenium centre is coordinated through a sigma bond to the amine N atom and two carbonyl ligands at the base of the stool and the cyclopentadienyl ring in the apex of the stool. IR studies showed that peaks of the νCO stretching vibrations shifted slightly to lower frequency as the carbon chain length increased. The melting point and percentage yields were observed to generally decrease with increase in n-value.

Keywords: Ruthenium alkanamine complexes; Crystal structure; Ruthenium carbonyl; Cyclopentadienyl ruthenium; Melting point trends

## 1. Introduction

Synthesis, characterization and reactions of organometallic complexes having metal-nitrogen bonds have not been widely reported [1] due to the general belief that the bond between the nitrogen ligand and late transition metals is relatively weak [2] and that complexes with nitrogen donors containing N-H bonds are generally unsuitable for organometallic reactions, as H atom(s) on the coordinating nitrogen are sufficiently acidic to react with nucleophiles [3]. Despite these beliefs, neutral aliphatic amine dicarbonyl cyclopentadienyl manganese(I) complexes are relatively well studied compared to other metals; and $CpMn(CO)_2(pip)$ ($Cp = \eta^5$-$C_5H_5$, pip = piperazine) [4]; $CpMn(CO)_2NH_2(CH_2)_2CH_3$ [5]; $CpMn(CO)_2(m\text{-}NH_2C_6H_4CH_3)$ [6]; and $CpMn(CO)_2$(pyrrolidine) are known [7]. Neutral 1-propanamine complexes of manganese and rhenium were prepared from an ethereal complex by the substitution of the labile ligand by n-propanamine [8]. Very few such compounds for group 8 transition metals had been reported [9-11]. Recently, amine dicarbonyl cyclopentadienyliron complexes [12,13] were prepared, but none for ruthenium have been reported.

The chemistry of water-soluble transition metal compounds has gained considerable prominence in recent years, not only because water is an environmentally and biologically benign solvent, but also because of their use in biphasic catalysis [14] and biomedicine [15]. Biologically, transition metals have been shown to exert therapeutic and diagnostic influence on certain diseases increasing impetus in the development of new water-soluble and in vivo-stable transition metal compounds [15,16]. As such, the compatibility of organometallic compounds with water is important for the development of biomedicines [17], bioorganometallic chemistry and organometallic radiopharmaceuticals.

Most compounds that are pharmacologically important have been nitrogen-containing organometallics such as, diaminoalkanes [18,19], ferrocenyl diamines [20] and ferrocenyl diaminoalcohols [21], which have shown high activity biologically. These compounds may also have exciting catalytic applications [22]. For this reason, we have decided to investigate the interaction of iron and ruthenium carbonyl complexes with nitrogen-containing species to develop the chemistry and also study the physiology and pharmacology of the resulting complexes. We recently reported iron complexes of the form $[CpFe(CO)_2NH_2R]BF_4$ (R = $CH_3$ **1**, $C_2H_5$ **2**, $C_3H_7$ **3**, $C_4H_9$ **4** and $C_5H_{11}$ **5**), synthesised from the ethereal complex salt, $[CpFe(CO)_2(CH_3CH_2)_2O]BF_4$ [12]. In this paper we report the synthesis and characterization of $CpRu(CO)_2NH_2R]BF_4$ (R = $CH_3$ **1**, $C_2H_5$ **2**, $C_3H_7$ **3**, $C_4H_9$ **4** and $C_5H_{11}$ **5**). The crystal structures

of complexes **2** – **5** are reported. To the best of our knowledge, 1-alkanamine complexes of the cyclopentadienyl dicarbonyl ruthenium(II) have not been previously reported. Furthermore, these new 1-alkanaminedicarbonyl($\eta^5$-cyclopentadienyl)ruthenium(II) complex salts are soluble and stable in water.

## 2. Experimental

### *2.1 General methods and materials*

Standard Schlenk techniques were employed for all reactions. Nitrogen gas (AFROX) was dried over phosphorus(V) oxide. Chemical reagents and solvents were obtained from the suppliers shown in parentheses: reagent grade $Et_2O$ (Merck) was distilled from sodium/benzophenone and stored over molecular sieves; methylene chloride (Merck) was distilled from phosphorous(V) oxide. Silver tetrafluoroborate (Alfa Aesar), ruthenium trichloride hydrate (DLD-Aldrich), dicyclopentadiene (Aldrich), n-propylamine, n-pentylamine, n-hexylamine (Merck), n-pentylamine (BDH), n-ethylamine, n-methylamine (Aldrich), carbon monoxide (AFROX) and iodine (Unilab) were used as supplied. Melting points were recorded on an Ernst Leitz Wetzlar hot-stage microscope and are uncorrected. Elemental analyses were performed on a Thermo-Scientific Flash 2000 CHNS/O analyser. Solid state infrared spectra were recorded using an FTIR Perkin Elmer Spectrum 100 spectrophotometer between 4000 and 400 $cm^{-1}$. Mass spectra were recorded on an Agilent 1100 series LC/MSD trap with electrospray ionization (ESI) source and quadrupole ion trap mass analyzer by direct infusion and ESI operated in the positive mode. Acetonitrile (100%) was used as mobile phase and 10 μL of the sample injected at 0.3 ml/min flow rate. NMR spectra were recorded on Bruker Topspin 400 and 600 MHz spectrometers. The deuterated solvents $CDCl_3$ (Aldrich, 99.8%), and $D_2O$ (Aldrich) were used as purchased. Solutions for NMR spectroscopy were prepared under nitrogen using nitrogen-saturated solvents. The precursors $Ru_3(CO)_{12}$ [23], $[CpRu(CO)_2]_2$ [24], $CpRu(CO)_2I$ [25], and $[Cp(CO)_2Ru]BF_4$ [26], were prepared by literature methods.

## *2.2 Synthesis of the 1-alkanaminedicarbonyl($\eta^5$-cyclopentadienyl)ruthenium(II) tetrafluoroborate complex salts*

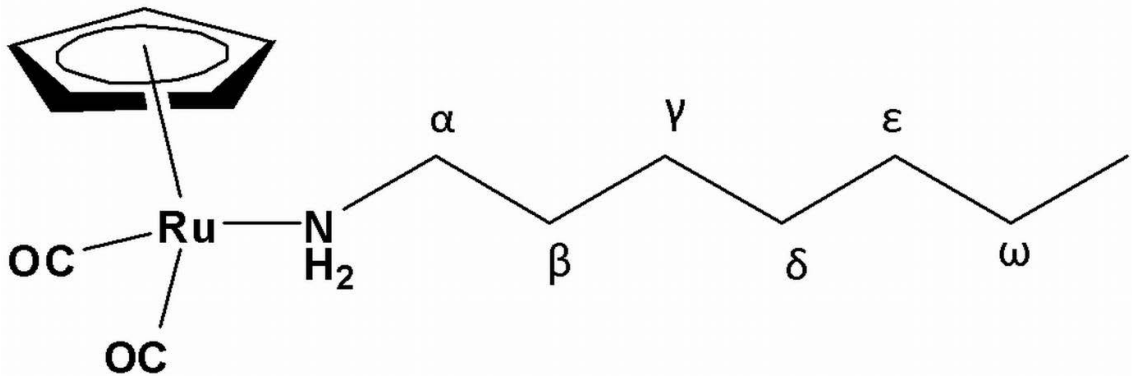



**Figure 1**: General structure of **1**-alkanaminedicarbonyl(η5-cyclopentadienyl)ruthenium(II) complex cation with carbon atoms on the alkyl chain labelled

### *2.2.1 Methanamine complex salt (**1**), $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_3]BF_4$*

RpI (0.1263 g; 0.3618 mmol) (Rp = $\eta^5$-$C_5H_5Ru(CO)_2$) and a magnetic stirrer bar were placed in a clean, dry Schlenk tube wrapped in aluminium foil and purged with dry, oxygen-free nitrogen gas. $AgBF_4$ (0.0872 g; 0.4479 mmol) was added and the tube evacuated at reduced pressure for 4 h to remove any moisture. It was filled with dry nitrogen gas, dry deoxygenated methylene chloride, 20 mL, was added and the mixture stirred for 1 ½ h. The resulting mixture was canula filtered under dry, oxygen-free nitrogen gas to give a white residue and an orange filtrate.

A slight excess of methylamine (0.400 mmol; 50 µL of 33 weight % methylamine in absolute ethanol) was added to the filtrate and stirred for 3 h. The colour of the solution changed from orange to yellow. The solution was allowed to remain undisturbed for 30 min. A black residue settled at the bottom of the Schlenk tube. The pale-yellow mother liquor was canula filtered into a clean, dry pre-weighed Schlenk tube. The filtrate was concentrated under reduced pressure. A four-fold volume of dry, oxygen-free diethyl ether was added to the pale yellow solution (2 mL) and a greyish-white precipitate was formed on shaking the mixture. The precipitate was allowed to settle and the mother liquor removed by canula filtration. The residue was re-dissolved in methylene chloride, allowed to stand for a few minutes and then canula filtered to remove a black residue. Diethyl ether was added to the filtrate to give a white precipitate. Canula filtration

gave a white solid which was washed twice with 10 mL portions of dry diethyl ether. The solid was dried under reduced pressure for 4 h to give 0.0998 g (82 %) of white powder. The solid decomposes after 178 °C. Anal. Found (calculated) for $C_8H_{10}NO_2RuBF_4$; C, 28.08 (28.26)%; H, 2.30 (2.96)%; N, 4.17 (4.12)%. NMR: (400 MHz; $CDCl_3$): $^1$H NMR δ 5.59 (s, 5H, Cp); δ 3.91 (s, 2H, $NH_2$); δ 2.63 (m, 3H, CH3). $^{13}$C NMR δ 195.18 (CO); δ 87.81 Cp); δ 41.42 ($CH_3$). NMR: (400 MHz; $D_2O$): $^1$H NMR δ 5.68 (s, 5H, Cp); δ 4.41 (s, 2H, $NH_2$); δ 2.51 (m, 3H, CH3). $^{13}$C NMR δ 195.99 (CO); δ 87.65 Cp); δ 40.28 ($CH_3$). IR (solid state): ν(CO) 2036, 1978 $cm^{-1}$, ν($CH_3$) 2953, 2917$cm^{-1}$; ν($NH_2$) 3321, 3276 $cm^{-1}$

### *2.2.2 1-Ethanamine complex salt (2), [$\eta^5$-$C_5H_5Ru(CO)_2$ $NH_2CH_2CH_3$ $BF_4$*

RpI (0.1760 g; 0.4956 mmol) and a slight excess of $AgBF_4$ (0.1276 g; 0.6554 mmol) was placed in a clean, dry Schlenk tube wrapped with aluminium foil and treated as described for the methylamine complex salt preparation. n-Ethanamine (0.6208 mmol of 2M n-ethylamine in THF) were added to the resulting orange solution and the mixture treated as described in Section 2.2.1 above. The product (0.1592 g) was formed in 89% yield. The melting range of the solid is 87-88 °C. Anal: Found (calculated) for $C_9H_{12}NO_2RuBF_4$; C, 30.49 (30.53)%; H, 3.14 (3.42)%; N, 4.01 (3.94)%. NMR: (400 MHz; $CDCl_3$): $^1$H NMR δ 5.59 (s, 5H, Cp); δ 3.88 (w, 2H, $NH_2$); δ 2.73 (m, 2H, $CH_2$); δ 1.20 (m, 3H, $CH_3$). $^{13}$C NMR δ 195.32 (CO); δ 87.83 Cp); 50.04 ($CH_2$); δ 17.49 ($CH_3$). NMR: (400 MHz; $D_2O$): $^1$H NMR δ 5.67 (s, 5H, Cp); δ 4.46 (w, 2H, $NH_2$); δ 2.73 (m, 2H, $CH_2$); δ 1.13 (m, 3H, $CH_3$). $^{13}$C NMR δ 196.08 (CO); δ 87.61 (Cp); 49.07 ($CH_2$); δ 17.01 ($CH_3$). IR (solid state): ν(CO) 2058, 1995 $cm^{-1}$, ν($C_5H_5$) 3126 $cm^{-1}$; ν($CH_3$) 2997 $cm^{-1}$, 2952 $cm^{-1}$; ν($NH_2$) 3325, 3286 $cm^{-1}$.

### *2.2.3 1-Propanamine complex salt (**3**), [$\eta^5$-$C_5H_5Ru(CO)_2NH_2(CH_2)_2CH_3]BF_4$*

RpI (0.26 g; 0.7448 mmol) and a magnetic stirrer bar were put in a clean, dry Schlenk tube and evacuated at reduced pressure for 2 h, then filled with dry nitrogen gas. Dry methylene chloride (15 mL) was added and the mixture stirred. At the same time, $AgBF_4$ (0.1864 g; 0.9575 mmol) and a magnetic stirrer bar were placed in a separate clean, dry Schlenk tube wrapped with aluminium foil and evacuated for 2 h, then filled with dry nitrogen gas. Methylene chloride (15 mL) was added to this and the mixture stirred. The RpI solution in methylene chloride was added to the stirring solution of $AgBF_4$. The mixture was stirred for 1½ h, a slight excess of n-propylamine (0.058 g; 0.9812 mmol) added and the mixture stirred for a further 3 h. The colour

of the solution changed from orange to yellow. The mixture was cannula filtered to give a yellow filtrate and a white precipitate. The solvent was evaporated under reduced pressure to give a greenish yellow solid. Methylene chloride (10 mL) was added to the solid and stirred to give a pale yellow solution and a grey precipitate. The solution was filtered into a clean, dry, pre-weighed Schlenk tube and the filtrate evaporated under reduced pressure to give a white solid. The solid was recrystallized from methylene chloride (5 mL) and excess diethylether added. White needle-shaped crystals (0.2055 g) were obtained in 75% yield. The melting point ranged from 109.2-109.6 °C.

Anal: Found (calculated) for $C_{10}H_{14}NO_2RuBF_4$; C, 31.98 (32.63)%; H, 3.98 (3.83)%; N, 3.42 (3.81)%. NMR: (400 MHz; $CDCl_3$): $^1$H NMR δ 5.59 (s, 5H, Cp); δ 3.89 (s, 2H, $NH_2$); δ 2.62 (m, 2H, α$CH_2$); δ 1.60 (m, 2H, β$CH_2$); δ 0.89 (t, 3H, $CH_3$). $^{13}$C NMR δ 195.41 (CO); δ 87.89 Cp); 57.25 (α$CH_2$); δ25.65 (β$CH_2$) δ 10.74 ($CH_3$). (600 MHz; $D_2O$): $^1$H NMR δ 5.64 (s, 5H, Cp); δ 4.42 (s, 2H, $NH_2$); δ 2.64 (m, 2H, α$CH_2$); δ 1.50 (m, 2H, β$CH_2$); δ 0.87 (t, 3H, $CH_3$). $^{13}$C NMR δ 196.15 (CO); δ 87.71 Cp); 56.44 (α$CH_2$); δ25.38 (β$CH_2$) δ 10.08 ($CH_3$). IR (solid state): ν(CO) 2061, 2009 $cm^{-1}$, ν($C_5H_5$) 3118 $cm^{-1}$; ν($CH_3$) 2967 $cm^{-1}$, 2876 $cm^{-1}$; ν($NH_2$) 3314, 3272 $cm^{-1}$.

### *2.2.4 1-Butanamine complex salt (**4**), [$\eta^5$-$C_5H_5Ru(CO)_2NH_2(CH_2)_3CH_3$ $BF_4$*

RpI (0.2194 g; 0.6285 mmol), excess $AgBF_4$ (0.7936 mmol) and a magnetic stirrer bar were placed in a clean, dry Schlenk tube wrapped with aluminium foil. The tube was evacuated for 3 h under reduced pressure to remove any moisture then filled with dry nitrogen gas. Methylene chloride (25 mL) was added, followed by a slight excess of 1-butanamine (0.9223 mmol) and the mixture stirred for 3 h. The resulting mixture was treated as described for the 1-propanamine complex in Section 2.2.3. The product was obtained in 72% yield (0.158 g). The melting point is 54-55 °C.

Analysis: Found (calculated) for $C_{11}H_{16}NO_2RuBF_4$; C, 33.98 (34.57)%; H, 3.98 (4.22)%; N, 3.42 (3.67)%. NMR: (400 MHz; $CDCl_3$): $^1$H NMR δ 5.59 (s, 5H, Cp); δ 3.85 (s, 2H, $NH_2$); δ 2.64 (m, 2H, α$CH_2$); δ 1.55 (m, 2H, β$CH_2$); δ 1.30 (m, 2H, γ$CH_2$); δ 0.87 (t, 3H, $CH_3$). $^{13}$C NMR δ 195.41 (CO); δ 87.85 Cp); 55.23 (α$CH_2$); δ34.30 (β$CH_2$); δ19.52 (γ$CH_2$); δ 13.59 ($CH_3$). NMR: (400 MHz; $D_2O$): $^1$H NMR δ 5.67 (s, 5H, Cp); δ 4.43 (s, 2H, $NH_2$); δ 2.68 (m, 2H, α$CH_2$); δ 1.49 (m, 2H, β$CH_2$); δ 1.33 (m, 2H, γ$CH_2$); δ 0.90 (t, 3H, $CH_3$). $^{13}$C NMR δ 196.09 (CO); δ 87.64 Cp); 54.50 (α$CH_2$); δ34.18 (β$CH_2$); δ19.00 (γ$CH_2$); δ 12.88 ($CH_3$). IR (solid

state): ν(CO) 2062, 1994 $cm^{-1}$, ν($C_5H_5$) 3110 $cm^{-1}$; ν($CH_3$) 2967 $cm^{-1}$, 2937 $cm^{-1}$; ν($NH_2$) 3322, 3280 $cm^{-1}$

### *2.2.5 1-Pentanamine complex salt (**5**), [$\eta_5$-$C_5H_5Ru(CO)_2NH_2(CH_2)_4CH3]BF_4$*

RpI (0.1544 g; 0.4423 mmol), excess $AgBF_4$ (0.1080 g; 0.5548 mmol) and a magnetic stirrer bar were placed in a clean, dry Schlenk tube wrapped in aluminium foil and treated as described for the n-butylamine complex. To the orange solution obtained after filtration, a slight excess of 1-pentanamine (0.0472 g; 0.5415 mmol) was added and the mixture stirred for 3 h. The colour changed from orange to greenish yellow. The resulting mixture was treated as described for the 1-butanamine complex and a white solid was obtained (0.1141 g; 65%). The solid melts at 81.6 °C.

Anal: Found (calculated) for $C_{12}H_{18}NO_2RuBF_4$; C, 35.98 (36.38)%; H, 4.02 (4.58)%; N, 3.42 (3.54)%. NMR: (600 MHz; $CDCl_3$): $^1$H NMR δ 5.60 (s, 5H, Cp); δ 3.89 (s, 2H, $NH_2$); δ 2.65 (m, 2H, α$CH_2$); δ 1.60 (m, 2H, β$CH_2$); δ 1.28 (m, 4H, γ and δ$CH_2$); δ 0.87 (t, 3H, $CH_3$). $^{13}$C NMR δ 195.43 (CO); δ 87.86 Cp); 57.51 (α$CH_2$); δ32.04 (β$CH_2$); δ28.43 (γ$CH_2$); δ22.21 (δ$CH_2$); δ 13.85 ($CH_3$). NMR: (400 MHz; $D_2O$): $^1$H NMR δ 5.66 (s, 5H, Cp); δ 4.46 (s, 2H, $NH_2$); δ 2.68 (m, 2H, α$CH_2$); δ 1.52 (m, 2H, β$CH_2$); δ 1.29 (m, 4H, γ and δ$CH_2$); δ 0.89 (t, 3H, $CH_3$). IR (solid state): ν(CO) 2053, 1997 $cm^{-1}$, ν($C_5H_5$) 3127 $cm^{-1}$; ν($CH_3$) 2942 $cm^{-1}$, 2866 $cm^{-1}$; ν($NH_2$) 3321, 3280 $cm^{-1}$.

### *2.2.6 1-Hexanamine complex salt (**6**), [$\eta^5$-$C_5H_5Ru(CO)_2NH_2(CH_2)_5CH_3]BF_4$*

RpI (0.4535 g; 1.30 mmol), $AgBF_4$ (0.2993 g; 1.54 mmol) and a magnetic stirrer bar were put in a clean, dry Schlenk tube wrapped with aluminium foil. The mixture was dried under reduced pressure for 3 h, and then the tube was filled with dry nitrogen gas. Dry methylene chloride (30 mL) was added and the mixture stirred for 1½ h. A white precipitate and an orange filtrate were obtained. The mixture was filtered into a clean dry Schlenk tube. A slight excess of 1-hexanamine (0.1850 g; 1.83 mmol) was added to the orange filtrate and stirred for 3 h. The solution changed colour from orange to greenish yellow. The mixture was left undisturbed for 1 hr and then cannula filtered into a pre-weighed, clean, dry Schlenk tube. A black residue was left, while the filtrate obtained was pale yellow. The volume of the solution was reduced under reduced pressure. Excess dry hexane was added to the saturated solution and a white precipitate

was formed. The mixture was filtered; the precipitate re-dissolved in dry methylene chloride and re-crystallized using dry hexane. The precipitate was washed twice with dry hexane and dried under vacuum for 4 h. The product was obtained in 62% yield (0.3329 g). The solid melted in a temperature range of 73-74 °C.

Anal: Found (calculated) for $C_{13}H_{20}NO_2RuBF_4$; C, 37.72 (38.07)%; H, 5.12 (4.91)%; N, 3.62 (3.41)%. NMR: (400 MHz; $CDCl_3$): $^1$H NMR δ 5.59 (s, 5H, Cp); δ 3.85 (s, 2H, $NH_2$); δ 2.64 (m, 2H, α$CH_2$); δ 1.29 (m, 8H, β, γ, δ and ε$CH_2$); δ 0.87 (t, 3H, $CH_3$). $^{13}$C NMR δ 195.40 (CO); δ 87.87 Cp); δ 55.58 (α$CH_2$); δ32.34 (β$CH_2$); δ 31.31(γ$CH_2$); δ 26.06 (δ$CH_2$); δ22.46 (ε$CH_2$); δ 13.93 ($CH_3$). (400 MHz; $D_2O$): $^1$H NMR δ 5.66 (s, 5H, Cp); δ 4.43 (s, 2H, $NH_2$); δ 2.68 (m, 2H, α$CH_2$); δ 1.50 (m, 8H, β, γ and δ$CH_2$); δ 1.31 (m, 2H, ε$CH_2$); δ 0.89 (t, 3H, $CH_3$). $^{13}$C NMR δ 196.08 (CO); δ 87.63 Cp); δ 54.52 (α$CH_2$); δ 31.89 (β$CH_2$); δ 30.62 (γ$CH_2$); δ 23.30(δ$CH_2$); δ 21.81(ε$CH_2$); δ 13.22 ($CH_3$). IR (solid state): ν(CO) 2057, 1999 cm$^{-1}$, ν($C_5H_5$) 3126 cm$^{-1}$; ν($CH_3$) 2958, 2928, 2856 cm$^{-1}$, ν($NH_2$) 3315, 3276 cm$^{-1}$

### *2.3 X-ray crystal structure determination of [CpRu(CO)$_2$NH$_2$(CH$_2$)$_n$CH$_3$]BF$_4$ (n=1-4)*

Crystals of [$CpRu(CO)_2NH_2(CH_2)_nCH_3$]$BF_4$ suitable for single crystal X-ray diffraction studies were grown by the liquid diffusion method. Solutions of the compounds in dry dimethyl chloride were layered with a fourfold volume excess of diethyl ether and allowed to stand undisturbed in the dark at room temperature for 24 hours. Crystals of the complex salts **2 - 5** were selected and glued on to the tip of glass fibres. The crystals were then mounted in a stream of cold nitrogen at 100(1) K and centred in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Smart APEXII diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a diffractometer to crystal distance of 4.00 cm. The initial cell matrix was obtained from three series of scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range with the exposure time of about 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite [27]. The final cell constants were calculated from a set of 6460 strong reflections from the actual data collection. Data collection method involved ω scans of width 0.5°. Data reduction was carried using the program SAINT+ [27]. The structure was solved by direct methods using SHELXS [28] and refined by SHELXL [27]. All structures were checked for solvent-accessible cavities using PLATON [29] and the graphics were performed with the DIAMOND [30] visual crystal structure information system software. Non-H atoms were first refined isotropically and then by anisotropic

refinement with full-matrix least-squares calculations based on $F^2$ using SHELXS [29]. All H atoms were positioned geometrically and allowed to ride on their respective parent atoms. The carboxyl H atoms were located from the difference map and allowed to ride on their parent atoms. All H atoms were refined isotropically. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [27]. Crystal data and structure refinement information for compounds **2** – **5** are summarized in Table 1.

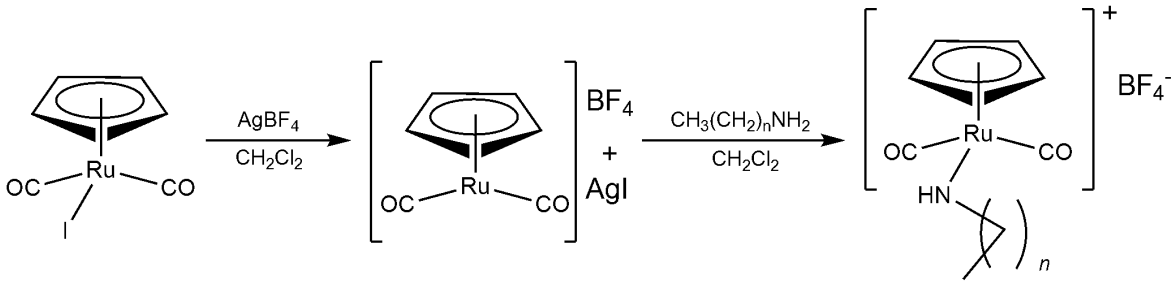
**Table 1**: Crystal data and structure refinement for compounds **2**, **3**, **4** and **5**

| | **2** | **3** | **4** | **5** |
|---|---|---|---|---|
| **Empirical formula** | $C_9H_{12}BF_4NO_2Ru$ | $C_{10}H_{14}BF_4NO_2Ru$ | $C_{11}H_{16}BF_4NO_2Ru$ | $C_{12}H_{18}BF_4NO_2Ru$ |
| **Formula weight** | 354.08 | 368.10 | 382.13 | 396.15 |
| **Temperature** | 173(2) K | 173(2) K | 173(2) K | 173(2) K |
| **Wavelength** | 0.71073 Å | 0.71073 Å | 0.71073 Å | 0.71073 Å |
| **Crystal system** | Orthorhombic | Monoclinic | Monoclinic | Monoclinic |
| **Space group** | Pbca | P21/c | P21/c | P21/c |
| **Unit cell dimensions (Å / °)** | a = 14.6686(5) Å, b = 11.3131(4) Å, c = 14.9801(6) Å, | a = 10.4412(2) Å, b = 7.69910(10) Å, β= 97.7450(10)°. c = 16.8002(3) Å, | a = 9.1329(5) b = 8.4964(4) Å, β = 112.154(2)°. c = 19.3325(9) Å, | a = 14.4432(3) Å, b = 14.1166(3) Å, β = 115.978(2)°. c = 17.0859(4) Å, |
| **Volume** | 2485.91(16) $Å^3$ | 1338.21(4) $Å^3$ | 1389.39(12) $Å^3$ | 3131.65(12) $Å^3$ |
| **Z** | 8 | 4 | 4 | 8 |
| **Density (calculated)** | 1.892 $Mg/m^3$ | 1.827 $Mg/m^3$ | 1.827 $Mg/m^3$ | 1.680 $Mg/m^3$ |
| **Absorption coefficient** | 1.303 $mm^{-1}$ | 1.214 $mm^{-1}$ | 1.173 $mm^{-1}$ | 1.044 $mm^{-1}$ |
| **F(000)** | 1392 | 728 | 760 | 1584 |
| **Crystal size** | 0.23 x 0.15 x 0.13 $mm^3$ | 0.47 x 0.26 x 0.15 $mm^3$ | 0.36 x 0.25 x 0.21 $mm^3$ | 0.13 x 0.23 x 0.50 $mm^3$ |
| **Theta range for data collection** | 2.65 to 28.40°. | 1.97 to 28.34°. | 2.41 to 25.00°. | 1.96 to 28.42°. |
| **Index ranges** | -19≤h≤19, -15≤k≤14, -19≤l≤19 | -13≤h≤13, -10≤k≤10, -22≤l≤21 | -10≤h≤10, -10≤k≤10, -22≤l≤19 | -19≤h≤19, -18≤k≤18, -22≤l≤22 |
| **Reflections** | 63059 | 28712 | 20134 | 52347 |

| | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| **collected** | | | | |
| **Independent reflections** | 3103 [R(int) = 0.0190] | 3325 [R(int) = 0.0203] | 2417 [R(int) = 0.0377] | 7542 [R(int) = 0.0329] |
| **Completeness to theta = 28.45°** | 99.6 % | 99.7 % | 98.9 % | 95.9 % |
| **Absorption correction** | Multi-scan | Multi-scan | Multi-scan | Multi-scan |
| **Max. and min. transmission** | 0.8489 and 0.7537 | 0.8389 and 0.5992 | 0.7908 and 0.6775 | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| **Data / restraints / parameters** | 3103 / 0 / 164 | 3325 / 0 / 173 | 2417 / 0 / 182 | 7542 / 0 / 381 |
| **Goodness-of-fit on $F^2$** | 1.076 | 1.156 | 1.301 | 1.131 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0148, wR2 = 0.0390 | R1 = 0.0161, wR2 = 0.0442 | R1 = 0.0262, wR2 = 0.0630 | R1 = 0.0257, wR2 = 0.0648 |
| **R indices (all data)** | R1 = 0.0164, wR2 = 0.0409 | R1 = 0.0172, wR2 = 0.0456 | R1 = 0.0275, wR2 = 0.0637 | R1 = 0.0372, wR2 = 0.0728 |
| **Largest diff. peak and hole** | 0.438 and -0.409 e.Å$^{-3}$ | 0.363 and -0.699 e.Å$^{-3}$ | 0.740 and -0.430 e.Å$^{-3}$ | 0.552 and -0.822 e.Å$^{-3}$ |

## 3. Results and discussion

### *3.1 Synthesis and characterization of $[CpRu(CO)_2NH_2R]BF_4$*




**1**, *n* = 0 (methylamine); **2**, *n* = 1 (ethylamine);
**3**, *n* = 2 (propylamine); **4**, *n* = 3 (butylamine);
**5**, *n* = 4 (pentylamine); **6**, *n* = 5 (hexylamine)

**Scheme 1:** Synthesis of 1-alkanaminedicarbonyl($\eta^5$-cyclopentadienyl)ruthenium(II) complex salts from $CpRu(CO)_2I$

The reaction of the organometallic Lewis acid, $[CpRu(CO)_2]^+$ (Cp = $\eta^5$-$C_5H_5$), with 1-alkanamines in dry methylene chloride at room temperature gives the new water-soluble 1-alkanamine complex salts of tetrafluoroborate, $[CpRu(CO)_2L]BF_4$ (L = $NH_2(CH_2)_nCH_3$). The complexes, $[CpRu(CO)_2L]BF_4$, form white, needle-shaped crystals that are air-stable and non-hygroscopic. The 1-alkanamine complexes are soluble in polar solvents such as methylene chloride, methanol, acetone, water and chloroform, but are insoluble in non-polar solvents such as hexane and diethyl ether. The yield of the complexes depends on the reaction duration and the length of the alkyl chain. The longer the chain, the longer the reaction time required to give a high yield. This could be due to increase in flexibility of the alkyl chain as the length increase. As the percentage yield decreases with increase in chain length, the iodine-bridged complex, $\{[CpRu(CO)_2]_2I\}BF_4$ [31], is simultaneously formed, from the competitive reaction between $CpRu(CO)_2I$ and $[CpRu(CO)_2]BF_4$. Similar observations were made in the synthesis of $[CpFe(CO)_2L]BF_4$ (L = $NH_2(CH_2)_nCH_3$) [12] where $\{[CpFe(CO)_2]_2I\}BF_4$ was simultaneously formed.

The melting points of the complexes were also found to decrease with increase in the n-alkylamine chain length probably due to decrease in the strength of the intermolecular interactions as the chain length increases. The complex salts with an even number of carbon atoms in the alkyl chain had relatively lower melting points compared to those with an odd number of carbon atoms. The odd numbered alkyl chained complexes have a higher packing efficiency in the solid phase, hence require more energy to weaken intermolecular interactions. This is in contrast to the classical observations reported for the melting point trends in the alkane series where, the even numbered alkanes have a higher melting point compared to the odd numbered ones [32].

The $^1H$ NMR data for the complexes **1** to **6** were obtained in $CDCl_3$ as well as $D_2O$ and peak assignments were done using 2D NMR. The $^1H$ NMR spectra in $CDCl_3$ showed a sharp singlet peak at ca. 5.59 ppm, assignable to the five equivalent cyclopentadienyl protons. A proton resonance singlet peak, observed at ca. 3.80 ppm, was assigned to the two amine protons. The amine proton peak was observed to be more down-field compared to those of the corresponding iron complexes, $[CpFe(CO)_2NH_2(CH_2)_nCH_3]BF_4$ [12]. These amine proton peaks were observed more down-field, a difference of about ca. 1.50 ppm from that of free 1-alkanamines (2.30 ppm), likely due to the de-shielding by the metal centre. This was a further indication of coordination of the 1-alkanamines to the metal centre through the N atom. In addition, there is a

possibility of hydrogen bonding between the amine group protons and the fluoride atoms of the tetrafluoroborate counter anion which can potentially contribute to the downfield shift of the amine protons in the $^{1}H$ NMR. The amine proton peak was observed to be more down-field in $D_2O$ (4.45 ppm) than in $CDCl_3$ likely due to hydrogen bond interaction between the amine protons and deuterium in $D_2O$. A multiplet at ca. 2.65 ppm was assigned to the protons on the α-carbon (Fig. 1) of the coordinated n-alkylamines. The α-carbon protons follow the same trend as the coordinated amine protons.

The $^{13}C$ NMR spectra for the complexes were recorded in $CDCl_3$ and peaks assigned by comparison with data reported for the cationic complexes $[CpFe(CO)_2NH_2(CH_2)_nCH_3]^+$ [12] and $[CpM(CO)_2(\eta^2\text{-}CH_2 = CHR)]^+$ [33] as well as HSQC experiments. There is a notably shift up-field in the methyl group carbon resonance signals as the chain length increases from n = 0 to n = 1 and then to n = 2, from 41.4 ppm to 17.5 and then to 10.9 ppm respectively (Table 2). This is probably because of a decrease in interaction with the amine group as the 1-alkanamine chain length increases. The methyl group carbon resonance signal for the 1-alkanamine complex salt does not change as the 1-alkanamine chain length increases from n = 3 onwards and occurs at ca.13.9 ppm, likely due to no further interaction of the methyl group with the amine. The methylene carbon resonance signals generally shift downfield due also to the deshielding effect caused by charge transfer by the alkyl group to the amine group [12]. The chain length does not affect the carbonyl and Cp carbon resonance signals, generally observed at ca. 195.4 ppm and ca. 87.9 ppm respectively. It is worth noting that the carbonyl carbon resonance signal for the ruthenium complexes, $[CpRu(CO)_2NH_2(CH_2)_nCH_3]^+$, is more upfield than in $[CpFe(CO)_2NH_2(CH_2)_nCH_3]^+$ (210.6 ppm). This is probably due to the higher electron density in the ruthenium nucleus, which in turn leads to greater charge transfer to the carbonyl group.

**Table 2:** $^{13}C$ NMR signals (ppm) for $[CpRu(CO)_2NH_2(CH_2)_nCH_3]BF_4$ ($CDCl_3$)

| n | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| **$\alpha CH_2$** | - | 50.0 | 53.3 | 55.3 | 55.5 | 55.6 |
| **$\beta CH_2$** | - | - | 25.6 | 34.3 | 32.0 | 32.3 |
| **$\gamma CH_2$** | - | - | - | 19.5 | 28.4 | 31.3 |
| **$\delta CH_2$** | - | - | - | - | 22.2 | 26.5 |
| **$\varepsilon CH_2$** | - | - | - | - | - | 22.5 |
| **$CH_3$** | 41.4 | 17.5 | 10.9 | 13.6 | 13.9 | 13.9 |

The IR spectra of the 1-alkanamine complexes **1** to **6** show two strong absorption bands in the νCO region between 2061 and 2036 $cm^{-1}$ assignable to the asymmetric CO stretching vibrations and between 2009 and1974 $cm^{-1}$ assignable to the symmetric CO stretching vibrations. It was observed that both sets of peaks of the νCO stretching vibrations shifted slightly to lower frequency as the carbon chain length increased. This could be attributed to steric and electronic effects of the alkyl chains towards the coordinated amine group. There is an increased electron back-donation to the carbonyl groups with increasing chain length leading to the shift to lower frequency [34]. Also noted were two weak bands in the ν(N–H ) region assignable to the N–H stretching modes between 3325 and 3311 $cm^{-1}$ for the asymmetric stretching and between 3280 and 3272 $cm^{-1}$ for the symmetric stretching modes. These bands showed a significant shift to lower wavenumbers when compared to the stretching frequencies of the unreacted starting 1-alkanamine further proving coordination to the Ru(II) centre. The observed shift could be attributed to charge transfer towards the metal centre through the coordinated nitrogen of the n-alkylamine. Back-donation of electrons by the metal centre to the coordinated carbonyl ligands leaves the methylene group electron deficient, hence the shift to lower wave numbers. A single absorption peak assignable to the N-H bending vibration is observed in the region 1596–1615 $cm^{-1}$.

Electrospray mass spectra of complexes **3**, **4** and **6** (Fig. 3) show the same fragmentation patterns. They lose the counter anion $BF_4^-$ to give the base peak of the 1-alkanamine complex cation $[CpRu(CO)_2NH_2(CH_2)_nCH_3]^+$, followed by successive loss of the carbonyl groups leaving the most stable fragment $[CpRuNH_2(CH_2)_nCH_3]^+$. No peaks associated with the fragment $[CpRu(CO)_2]^+$ were observed. These observations suggest that the n-alkylamine is strongly coordinated to the metal centre, while the CO groups are readily lost. The multiple peaks associated with the seven stable isotopes of ruthenium are clearly observed in each fragment (Fig. 2).

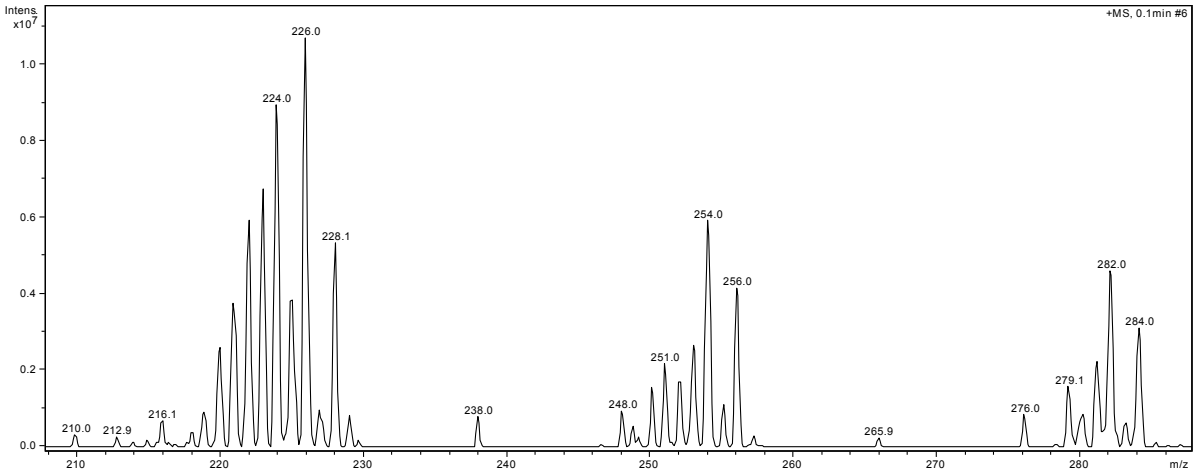



**Figure 2**: ES-MS spectrum showing the fragmentation pattern of $[CpRu(CO)_2NH_2(CH_2)_2CH_3]BF_4$

### *3.2 Crystal and molecular structures*

The structures of complexes **2**–**5** were determined using single crystal X-ray diffraction. All four compounds crystallize as white needle-like crystals. The molecular diagrams of the complexes are provided in Figs. 3–6, while Table 3 gives a comparison of important bond distances and angles.

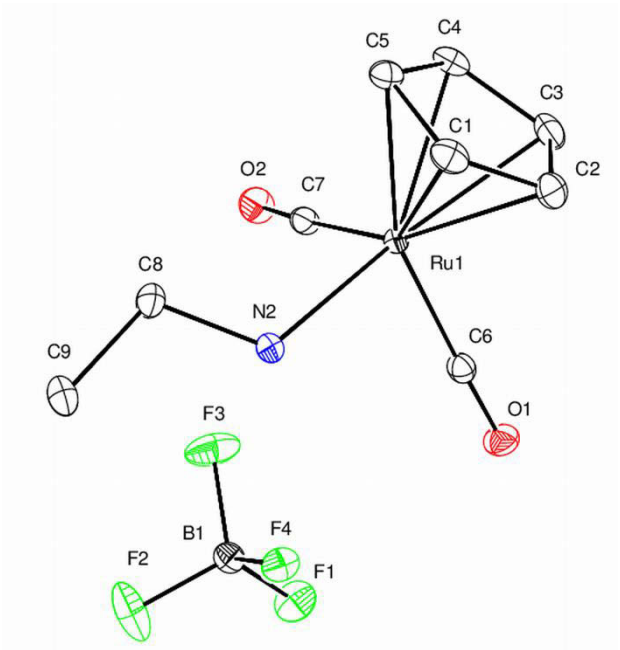



**Figure 3:** The structure of compound **2** showing the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level and H atoms have been omitted for clarity

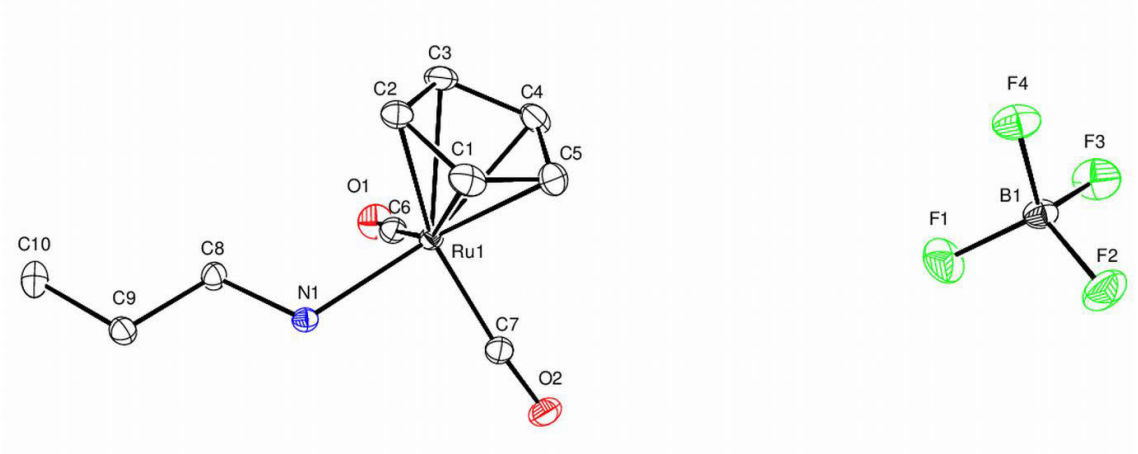



**Figure 4:** The structure of compound **3** showing the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level and H atoms have been omitted for clarity

Complexes **2**–**4** each crystallize with one molecule of the cation $[(\eta^5\text{-}C_5H_5)(CO)_2Ru(NH_2)L)]^+$ and a counter anion $BF_4^-$ in their asymmetric units, while complex **5** crystallizes with two molecules of the cation $[(\eta^5\text{-}C_5H_5)(CO)_2Ru(NH_2(CH_2)_4CH_3)]^+$ and two $BF_4^-$ counter anions in the unit cell. All of the four cationic species of the complexes feature the known "pseudo-octahedral three-legged piano stool" structures very similar to those of previously reported iron analogues $[CpFe(CO)_2NH_2(CH_2)_2CH_3]^+BF_4^-$ and $[CpFe(CO)_2NH_2(CH_2)_3CH_3]^+BF_4^-$ [12]. In this arrangement, the ruthenium center is coordinated through a sigma bond to the amine N atom and two carbonyl ligands at the base of the stool and by the cyclopentadienyl ring in the apex of the stool. The 1-alkanamine moiety seems to have a generally planar conformation with the exception of molecule 1 of compound **5,** which has a kink at the end of 1-pentanamine moiety (Fig. 6 and Table 3). This molecule has a reduced C9–C10–C11 torsional angle of 64.2(3) compared to analogous alkyl chain ends in the second molecule of compound **5**, as well as compounds **2**–**4** which range between 171.5 and 179.5° [35].

The Ru–N bond distances show only a slight increase from 2.139(1) to 2.148(2) Å as the amine chain length increases from n = 1 to n = 4. The bond distance is, however, comparable to Ru–N bonds of similar compounds, but significantly longer than those of analogous iron based compounds $CpFe(CO)_2NH_2(CH_2)_nCH_3]BF_4$ (2.013-2.018 Å) [12].

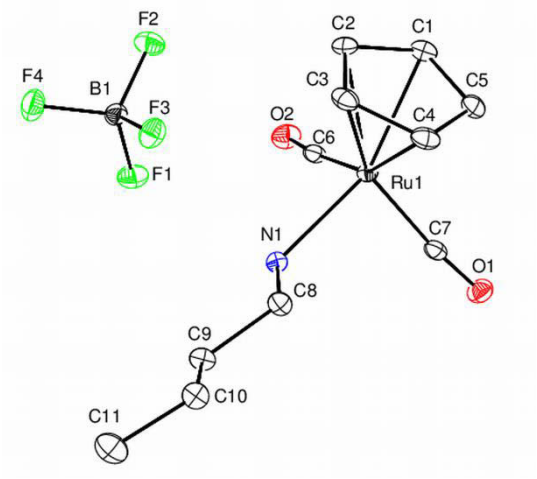



**Figure 5:** The structure of compound **4** showing the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level and H atoms have been omitted for clarity

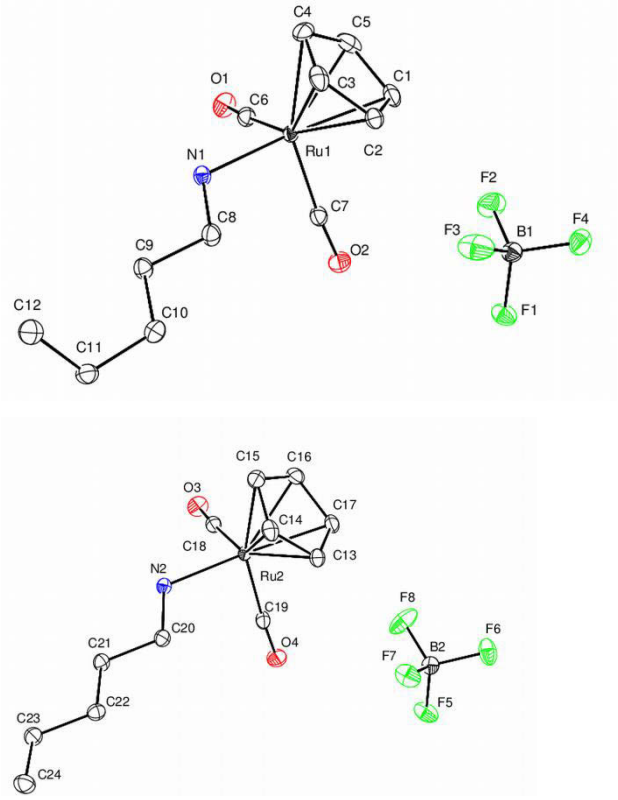



**Figure 6:** The structures of the two sets of molecules of compound **5** in the asymmetric unit showing the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level and H atoms have been omitted for clarity

In the crystal, molecules of **2**, **3**, **4** and **5** generally adopt the energetically favoured gauche type conformation in which the α-carbon of the 1-alknamine lies between a CO ligand and the cyclopentadienyl ring as shown in Fig. 7.

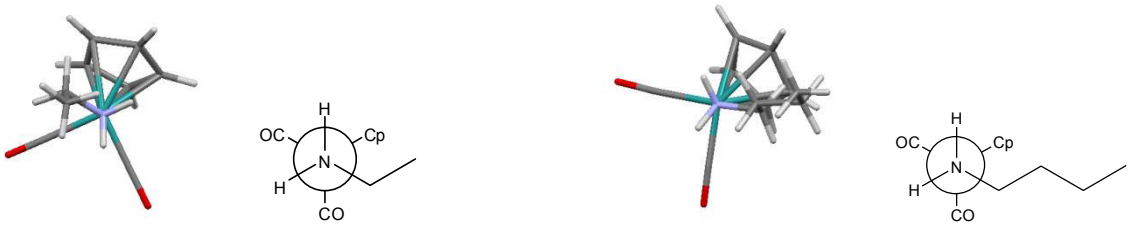



**Figure 7:** Gauche type conformation in compounds **2** and **4**

**Table 3:** Selected bond distances (Å) and angles ( °) for compounds **2**, **3**, **4** and **5**

| | **2** | **3** | **4** | **5a** | **5b** |
|---|---|---|---|---|---|
| *Cg−Ru | 1.8767(6) | 1.8804(7) | 1.8747(17) | 1.8737(12) | 1.8698(13) |
| Ru1−N1 | 2.139(1) | 2.1406(12) | 2.143(3) | 2.145(2) | 2.148(2) |
| C8−C9 | 1.485 | 1.483 | 1.491 | 1.487 | 1.489 |
| C6−Ru1 | 1.896(1) | 1.895(1) | 1.896(3) | 1.897(2) | 1.897(2) |
| C7−Ru1 | 1.907(1) | 1.896(1) | 1.896(4) | 1.902(2) | 1.902(2) |
| | | | | | |
| *Cg−Ru1−N1 | 123.48(4) | 122.92(4) | 124.08(9) | 123.99(7) | 124.07(7) |
| Ru1−N1−C8 | 118.53(8) | 115.06(8) | 117.5(2) | 116.4(8) | 116.4(8) |
| N1−C8−C9 | 111.6(1) | 113.9 | 111.7 | 113.2(2) | 113.2(2) |
| OC−Ru−CO | 90.89 | 89.56 | 92.76 | 91.51 | 91.33 |
| | | | | | |
| *Cg−Ru1−N1−C8 | 78.68 | 85.52 | –44.19 | –78.85 | –78.85 |
| | | | | | |
| Ru1−N1−C8−C9 | 171.40(8) | 174.58 | 173.0(2) | 173.9(1) | 172.2(1) |
| N1−C8−C9−C10 | – | 179.2(1) | 171.4(3) | 178.6(2) | 170.5(2) |
| C8−C9−C10−C11 | – | – | 175.8(3) | 176.7(2) | 177.8(2) |
| C9−C10−C11−C12 | – | – | – | 64.23 | 173.7 |

Cg is the centroid for C1-C5 of the Cp ring

All four compounds feature fairly strong N−H···F and C−H···F intermolecular interactions (Table 4). In the crystal structure of compound **2**, there is an additional π···π intermolecular interaction (Cg···Cg = 3.9760(9) Å, symmetry code = 1-x, 1-y, 1-z) that connects pairs of molecules that are related through an inversion centre. The cationic species are connected to the anionic species through three N−H···F and one C−H···F intermolecular interaction. Molecules in the crystal lattice of compound **3** are held together through one N−H···F, three C−H···F and a C−H···O intermolecular interaction. The crystal lattices of compounds **4** and **5** are dominated by N−H···F and C−H···F intermolecular interactions.

**Table 4:** Important intermolecular interactions and symmetry codes of the complex salts' crystal structures

| C-H…X | D–H | H…A | D…A | D–H…A | Symmetry codes |
|---|---|---|---|---|---|
| **2** | | | | | |
| N2−H2a···F1 | 0.92 | 2.33 | 3.1170(15) | 143 | 3/2-x, -½+y, z |
| N2−H2a···F3 | 0.92 | 2.27 | 3.1442(15) | 158 | 3/2-x, -½+y, z |
| N2−H2b···F4 | 0.92 | 2.00 | 2.8928(13) | 164 | x, y, z |
| C1−H1···F1 | 1.00 | 2.47 | 3.3305(16) | 143 | 3/2-x, -½+y, z |
| **3** | | | | | |
| N1−H1b···F4 | 0.99 | 2.07 | 2.9456(13) | 147 | x, y, z |
| C2−H2···F2 | 1.00 | 2.54 | 3.4765(19) | 155 | x, y, z |
| C3−H3···F2 | 1.00 | 2.42 | 3.4265(17) | 154 | -1+x,- ½-y, -½+z |
| C5−H5···F3 | 1.00 | 2.42 | 3.2631(19) | 142 | 1-x, ½+y, ½-z |
| C8−H8b···O1 | 0.99 | 2.60 | 3.4764(17) | 148 | 2-x, -½+y, 3/2-z |
| **4** | | | | | |
| N1−H1a···F1 | 0.92 | 2.34 | 3.106(3) | 141 | 1-x, 1-y, 2-z |
| N1−H1b···F1 | 0.92 | 2.35 | 3.175(3) | 149 | x, y, z |
| N1−H1b···F3 | 0.92 | 2.20 | 3.976(3) | 141 | x, y, z |
| C1−H1···F2 | 1.00 | 2.31 | 3.295(4) | 169 | 2-x, 1-y, 2-z |
| C3−H3···F4 | 1.00 | 2.48 | 3.357(4) | 147 | 1-x, ½+y, 3/2-z |
| C8−H8b···F4 | 0.99 | 2.53 | 3.387(4) | 144 | x, 1+y, z |
| **5** | | | | | |
| N1−H1a···F1 | 0.90 | 2.09 | 2.940(3) | 158 | x, ½-y, -½+z |
| N1−H1b···F7 | 0.90 | 2.39 | 3.258(3) | 162 | -1+x, ½-y, -½+z |
| N2−H2a···F5 | 0.90 | 2.20 | 2.972(3) | 143 | x, ½-y, -½+z |

| C-H…X | D–H | H…A | D…A | D–H…A | Symmetry codes |
|---|---|---|---|---|---|
| N2—H2b···F4 | 0.90 | 2.13 | 2.920(3) | 146 | x, ½-y, -½+z |
| C3—H3···F4 | 0.98 | 2.27 | 3.230(3) | 166 | x, ½-y, -½+z |
| C4—H4···F1 | 0.98 | 2.34 | 3.208(3) | 147 | 1-x, -½+y, ½-z |
| C13—H13···F7 | 0.98 | 2.54 | 3.448(3) | 154 | x, y, z |
| C14—H14···F6 | 0.98 | 2.30 | 3.224(3) | 157 | x, ½-y, -½+z |
| C15—H15···F5 | 0.98 | 2.35 | 3.188(3) | 144 | x, -½-y, ½-z |

## *4. Conclusion*

The stable and water soluble 1-alkanaminedicarbonyl($\eta^5$-cyclopentadienyl)ruthenium(II) complex salts, $[CpRu(CO)_2NH_2(CH_2)_nCH_3]^+BF_4^-$ (Cp= $\eta^5$-$C_5H_5$, n=0-5) have been successfully synthesized. Their IR data has shown that the carbonyl peak shifts to lower frequency as the alkyl chain increases. The $^1H$ and $^{13}C$ NMR data has shown that the 1-alkanamine is σ-bonded to the metal centre via nitrogen as the donor atom. This is further confirmed by the X-ray crystal structure, which also reveals gauche conformation responsible for stability of the cationic complex. The molecules are held together by N–H…F and C–H…F bonds, which enhance their stability and solubility in water. There is a general decrease in melting point of the 1-alkanamine complex salts as the alkyl chain increases.

**Acknowledgements**

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**Appendix A. Supplementary material**

CCDC 974499 - 974502 contains the supplementary crystallographic data for compounds **2**, **3**, **4** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/dat_request/cif .

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# CHAPTER FOUR

## Synthesis, characterization and structural elucidation of $\eta^5$-pentamethylcyclopentadienyldicarbonylrutheniuml(II) complex salts of 1-alkanamine

Eunice A. Nyawade and Holger B. Friedrich*

*Corresponding author

School of Chemistry and Physics, University of KwaZulu-Natal, Private Bag X54001, Durban 4000, South Africa

**Abstract**

Five new 1-alkanaminedicarbonyl($\eta^5$-pentamethylcyclopentadienyl)ruthenium(II) tetrafluoroborate complex salts, $[Cp^*Ru(CO)_2NH_2(CH_2)_nCH_3]BF_4$ ($Cp^* = \eta^5$-$C_5(CH_3)_5$; n = 0 (**1**), 1 (**2**), 2 (**3**), 3 (**4**) and 4 (**5**)) have been synthesized by the reaction of the Lewis acid $[Cp^*Ru(CO)_2]BF_4$ with a slight excess of the 1-alkylamines in dry methylene chloride. The water-soluble complexes are reported for the first time and have been characterized by IR, NMR and high resolution mass spectrometry. The 1-alkylamines are linked to the ruthenium centre by a sigma bond via the nitrogen atom of $NH_2$. The crystal structure of the complex $[Cp^*Ru(CO)_2NH_2CH_2CH_3]BF_4$ (**2**) was obtained by single crystal X-ray diffraction. It crystallizes in the triclinic crystal system, space group P-1.

Key words: Pentamethylcyclopentadienyl ruthenium, 1-aminoalkanes, Ruthenium alkanamine complexes, Alkanaminedicarbonyl($\eta^5$-pentamethylcyclopentadienyl)ruthenium(II)

### 1. Introduction

$\eta^5$-Pentamethylcyclopentadienyl ruthenium complexes have been known for more than four decades and have been shown to be potential catalysts in various organic transformations. The complex $[Cp^*Ru(NCCH_3)_3]PF_6$ ($Cp^* = \eta^5$-$C_5(CH_3)_5$), for example, was shown to catalyze the allylic alkylation of stabilized nucleophiles with high regioselectivity for addition at the more

substituted allyl terminal [1]. The complex [Cp*Ru(bpy)Cl] effectively catalyzed the formal [3,3] rearrangement of allyl β-ketoesters [2], while the Cp* ruthenium dicarbonyl complex, $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+Otf^-$ (Otf = $OSO_3CF_3$) was shown to selectively catalyze the deoxygenation of diols to alcohols, e.g. 1,2-propanediol to n-propanol [3,4].

The synthesis of ruthenium complexes of the $[Cp^*Ru(CO)_2]$ moiety with a variety of ligands have been reported. For example, the Cp* ruthenium dicarbonyl complex $K[Cp^*Ru(CO)_2]$ was synthesized by the reduction of $[Cp^*Ru(CO)_2]_2$ with potassium dispersed in sodium [5]. The reaction of this complex, $K[Cp^*Ru(CO)_2]$, with HCl, MeI, $MeOCH_2Cl$, $HSiCl_3$ and t-$BuPCl_2$ to form the corresponding complexes $[Cp^*Ru(CO)_2H]$, $[Cp^*Ru(CO)_2CH_3]$, $[Cp^*Ru(CO)_2CH_2OCH_3]$, $[Cp^*Ru(CO)_2HSiCl_2]$ and $[Cp^*Ru(CO)_2$t-BuPCl] was reported [5]. The Cp* ruthenium(II) dicarbonyl complexes, $[Cp^*Ru(CO)_3]BF_4$, $[Cp^*Ru(CO)_2CH_2OCH_3]$, $[Cp^*Ru(CO)_2H]$ and $[Cp^*Ru(CO)_2CH_2OH]$ are also known [6]. The complex $[Cp^*Ru(CO)_2(=CHOCH_3)]PF_6$ was obtained by α-hydride abstraction from $[Cp^*Ru(CO)_2CH_2OCH_3]$ by $PH_3CPF_6$ [7,8].

The Cp* ruthenium carbonyl complexes can, therefore, exist as neutral complex molecules or complex salts with weakly coordination counter anions such as $BF_4^-$, $PF_6^-$, $SO_3CF_3^-$, $BPh_4^-$ and $SbF_6^-$ or as $[Cp^*Ru(CO)_2]^-$ anionic salts of monovalent metals such as Li, Na or K.

Complexes of the type $[Cp^*Ru(CO)_2L]$ (L = nitrogen containing ligands), where the ligand is coordinated to the metal through the nitrogen atom are, however, not known. As part of the ongoing study on the coordination of amine ligands to the metal centre of $[CpM(CO)_2]$ (Cp = $\eta^5$-$C_5H_5$) (M = Fe or Ru) and $[Cp^*Fe(CO)_2]$ moieties, our group recently reported on the synthesis, characterization and crystal structures of $[CpFe(CO)_2(amines)]BF_4$, $[Cp^*Fe(CO)_2(amines)]BF_4$ [9-11] and $CpRu(CO)_2$1-alkanamines]$BF_4$ [12,13] complexes. We herein now report the synthesis and characterization of the five new, water-soluble complexes, $[Cp^*Ru(CO)_2NH_2(CH_2)_nCH_3]BF_4$ (n = 0 (**1**), 1 (**2**), 2 (**3**), 3 (**4**) and 4 (**5**)), and the crystal structure of $[Cp^*Ru(CO)_2NH_2CH_2CH_3]BF_4$ (**2**). To the best of our knowledge $\eta^5$-pentamethylcyclopentadienyldicarbonylruthenium(II) complexes of 1-alkylamines have not been reported before. The solubility of these complexes in water makes them suitable candidates for applications in biphasic catalysis, bioorganometallic chemistry and medicinal chemistry.

## 2. Experimental

### *2.1 General*

All manipulations were done under dry and oxygen-free conditions, unless otherwise stated. Reagent grade $Et_2O$, methylene chloride, n-propylamine and n-pentylamine were obtained from Merck; silver tetrafluoroborate, ruthenium trichloride hydrate, pentamethylcyclopentadiene, n-ethylamine (2 M in THF) and n-methylamine (33 weight% in absolute ethanol) were obtained from Aldrich; nitrogen and carbon monoxide gases were obtained from AFROX. Nitrogen was dried over phosphorus(V) oxide, $Et_2O$ was distilled from sodium/benzophenone and stored over molecular sieves, while methylene chloride was distilled from phosphorous(V) oxide. All other chemicals were used as supplied. Melting points were recorded on a Stuart Scientific melting point apparatus SMP3 and are uncorrected. Solid state infrared spectra were recorded using an ATR Perkin Elmer Spectrum 100 spectrophotometer between 4000 and 400 $cm^{-1}$. NMR spectra were recorded on Bruker Topspin 400 and 600 MHz spectrometers. The deuterated solvent $CDCl_3$ (Aldrich, 99.8%) was used as purchased. Solutions for NMR spectroscopy were prepared under nitrogen using nitrogen-saturated solvents. The high resolution mass spectra for the complexes were recorded on a Waters Synapt G2 instrument by injecting via the ESI probe into a stream of methanol. $[Cp^*Ru(CO)_2]_2$ was prepared by a modified literature method [14]. Best results were obtained when excess $C_5Me_5H$ is refluxed over $Ru_3(CO)_{12}$ in n-decane at 160 °C for 6 h. Orange crystals of $[Cp^*Ru(CO)_2]_2$ (0.2 g; 3.4 mmol) were dissolved in $CH_2Cl_2$ (20 mL) and an equimolar amount of iodine in $CH_2Cl_2$ (10 mL) added. Evaporation of the solvent under reduced pressure gave an orange solid of $Cp^*Ru(CO)_2I$ [15].

### *2.2 Synthesis of complexes $[Cp^*Ru(CO)_2NH_2(CH_2)_nCH_3]BF_4]BF_4$ (1 - 5)*

The synthesis of all the $\eta^5$-pentamethylcyclopentadienyldicarbonylruthenium(II) complexes, $[Cp^*Ru(CO)_2NH_2(CH_2)_nCH_3]BF_4]BF_4$, was achieved by a common procedure illustrated by the generic method for the synthesis of $[Cp^*Ru(CO)_2NH_2CH_3]BF_4$.

#### *2.2.1 $[Cp^*Ru(CO)_2NH_2CH_3]BF_4$ (**1**)*

$Cp^*Ru(CO)_2I$ (0.0525 g; 0.1270 mmol) and $AgBF_4$ (0.0296 g; 0.1520 mmol) were placed in an aluminium foil-wrapped Schlenk tube and evacuated under reduced pressure for 4 h to remove any traces of moisture. Methylene chloride (15 mL) was added to the Schlenk tube and the

mixture stirred for 1½ h. The mixture was canula filtered and excess (1.0 mmol; 125 µL) n-methylamine (33% weight in absolute ethanol) was added to the filtrate and the mixture stirred for 4 h. The colour of the mixture changed from orange to pale yellow. The solution was allowed to remain undisturbed for 30 min. The mother liquor was then transferred into a Schlenk tube by canula filtration. The pale yellow solution was concentrated under reduced pressure and a five-fold quantity of diethyl ether added. A pale-yellow gelatinous precipitate formed on shaking the mixture and this was then allowed to settle to the bottom of the Schlenk tube and the mother liquor removed by canula filtration. The residue was re-dissolved in $CH_2Cl_2$ (2 mL) and filtered to remove any solid impurities. Addition of excess diethyl ether gave a white precipitate, which was washed with diethyl ether (2 x 10 mL). The white precipitate was dried under reduced pressure for 4 h. The white solid (0.0370 g) was obtained in 72% yield. The solid turns black at 165 °C and then melts at 167.3 °C. Anal: Found (calculated) for $C_{13}H_{20}NO_2RuBF_4$; C, 37.68 (38.07)%; H, 5.23 (4.91)%; N, 3.91 (3.41)%. HRMS: Found (calculated) for $(C_{13}H_{20}NO_2Ru)^+$, $M^+$ 100%; 324.0528 (324.0538), 59%; 326.0545 (326.0548), 54.1%; 323.0545 (323.0550). IR (solid state): $\nu_{max}/cm^{-1}$ 2034, 1976 (CO); 2953, 2914 ($CH_3$); 3321, 3276, 1593 ($NH_2$). $\delta_H$ (400 MHz; $CDCl_3$): 3.36 (s, 2H, $NH_2$), 2.62 (t, 3H, CH3), 1.95 (s, 15H, $C(CH_3)_5$. $\delta_C$ (400 MHz; $CDCl_3$): 197.88 (CO), 100.24 $\underline{C}(CH_3)_5$, 40.73 ($CH_3$), 10.45 $C(\underline{C}H_3)_5$.

### *2.2.2 [Cp*Ru(CO)$_2$NH$_2$CH$_2$CH$_3$]BF$_4$ (**2**)*

The solid turns black at 158 °C and then melts 162 °C. Yield: (0.0416 g; 67%). Anal: Found (calculated) for $C_{14}H_{22}NO_2RuBF_4$; C, 36.68 (36.64)%; H, 5.20 (5.23)%; N, 3.27 (3.30)%. HRMS: Found (calculated) for $(C_{14}H_{22}NO_2Ru)^+$, $M^+$ 100%; 338.0686 (338.0694), 59%; 340.0703 (340.0705), 54.1%; 337.0702 (337.0706). IR (solid state): $\nu_{max}/cm^{-1}$ 2034, 1980 (CO), 2978 $cm^{-1}$, 2934 ($CH_3$), 3312, 3282, 1607 ($NH_2$). $\delta_H$ (400 MHz; $CDCl_3$): 3.30 (s, 2H, $NH_2$), 2.73 (m, 2H, $\alpha CH_2$), 1.22 (t, 3H, $CH_3$), 1.95 (s, 15H, $C(CH_3)_5$. $\delta_C$ (400 MHz; $CDCl_3$): 198.00 (CO), 100.26 $\underline{C}(CH_3)_5$, δ 49.12 ($CH_2$), δ 17.42 ($CH_3$), δ 9.61 $C(\underline{C}H_3)_5$.

### *2.2.3 [Cp*Ru(CO)$_2$NH$_2$(CH$_2$)$_2$CH$_3$]BF$_4$ (**3**)*

The solid turns black at 148 °C and then melts at 150 °C. Yield: (0.0293 g; 40%). Anal: Found (calculated) for $[C_{15}H_{24}NO_2RuBF_4$; C, 41.21 (41.11)%; H, 5.48 (5.52)%; N, 3.28 (3.20)%. HRMS: Found (calculated) for $(C_{15}H_{24}NO_2Ru)^+$, $M^+$ 100%; 352.0838 (3352.0851), 59%;

354.0857 (354.0861), 54.1%; 351.0862 (351.0863). IR (solid state): $\nu_{max}/cm^{-1}$ 2032, 1974 (CO); 2966, 2940(sh), 2882(sh) ($CH_3$); 3318, 3275, 1604 ($NH_2$). $\delta_H$ (400 MHz; $CDCl_3$): 3.30 (s, 2H, $NH_2$), 2.59 (m, 2H, $\alpha CH_2$), 1.62 (m, 2H, $\beta CH_2$), 0.88 (t, 3H, $CH_3$), 1.95 (s, 15H, $C(CH_3)_5$. $\delta_C$ (400 MHz; $CDCl_3$): 197.94 (CO), 100.24 $\underline{C}(CH_3)_5$, 56.26 ($\alpha CH_2$), 25.43 ($\beta CH_2$), 10.88 ($CH_3$), 9.61 $C(\underline{C}H_3)_5$.

### *2.2.4 [Cp*Ru(CO)$_2$NH$_2$(CH$_2$)$_3$CH$_3$]BF$_4$ (**4**)*

The solid turns black at 138 °C and then melts at 140 °C. Yield: (0.0241 g; 37%). Anal: Found (calculated) for $C_{16}H_{26}NO_2RuBF_4$; C, 42.68 (42.49)%; H, 5.82 (5.79)%; N, 3.13 (3.10)%. IR (solid state): $\nu_{max}/cm^{-1}$ 2029, 1975 (CO), 2964, 2935, 2875 ($CH_3$), 3309, 3271, 1600 ($NH_2$). $\delta_H$ (400 MHz; $CDCl_3$) 3.24 (s, 2H, $NH_2$), 2.63 (m, 2H, $\alpha CH_2$), 1.58 (m, 2H, $\beta CH_2$), 1.28 (m, 2H, $\gamma CH_2$), 0.89 (t, 3H, $CH_3$), 1.95 (s, 15H, $C(CH_3)_5$. $\delta_C$ (400 MHz; $CDCl_3$): 197.87 (CO), 100.26 $\underline{C}(CH_3)_5$, 54.18 ($\alpha CH_2$), 34.08 ($\beta CH_2$), 19.69 ($\gamma CH_2$), 13.60 ($CH_3$), 9.64 $C(\underline{C}H_3)_5$.

### *2.2.5 [Cp*Ru(CO)$_2$NH$_2$(CH$_2$)$_4$CH$_3$]BF$_4$ (**5**)*

The solid turns black at 152 °C and melts at 154 °C. Yield: (0.0348 g; 27%). Anal: Found (calculated) for $C_{17}H_{28}$ $NO_2RuBF_4$; C, 43.70 (43.79)%; H, 5.98 (6.05)%; N, 3.13 (3.00)%. IR (solid state): $\nu_{max}/cm^{-1}$ 2030, 1980 (CO), 2948, 2873($CH_3$), 3309, 3271 ($NH_2$) 1601 ($NH_2$). $\delta_H$ (400 MHz; $CDCl_3$): 3.31 (s, 2H, $NH_2$), 2.61 (m, 2H, $\alpha CH_2$), 1.61 (m, 4H, $\beta,\gamma CH_2$), 1.26 (m, 2H, $\varepsilon CH_2$), 0.86 (t, 3H, $CH_3$), 1.95 (s, 15H, $C(CH_3)_5$. $\delta_C$ (400 MHz; $CDCl_3$): 197.92 (CO), 100.27 $\underline{C}(CH_3)_5$, 54.45 ($\alpha CH_2$), 31.86 ($\beta CH_2$), 28.66 ($\gamma CH_2$), 22.23 ($\varepsilon CH_2$), 13.90 ($CH_3$), 9.71 $C(\underline{C}H_3)_5$.

## *2.3 X-ray crystal structure determination of [CpRu(CO)$_2$NH$_2$(CH$_2$)CH$_3$]BF$_4$*

Crystals of the complex $[Cp^*Ru(CO)_2NH_2(CH_2)CH_3]BF_4$ (**2**) suitable for single crystal X-ray diffraction studies were grown by the liquid diffusion method. Solutions of the compounds in dry methylene chloride were layered with a fourfold volume of diethyl ether and allowed to stand undisturbed in the dark at 22 °C for 24 h. Crystals of the complex salt **2** was selected and glued on to the tip of glass fibres. The crystals were then mounted in a stream of cold nitrogen at 100(1) K and centred in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker Smart APEXII diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a diffractometer to crystal distance of 4.00 cm. The initial cell matrix was

obtained from three series of scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range with the exposure time of about 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite [16]. The final cell constants were calculated from a set of 6460 strong reflections from the actual data collection. Data collection method involved ω scans of width 0.5°. Data reduction was carried using the program SAINT+ [16]. The structure was solved by direct methods using SHELXS [17] and refined by SHELXL [16]. All structures were checked for solvent-accessible cavities using PLATON [18] and the graphics were performed with the DIAMOND [19] visual crystal structure information system software. Non-H atoms were first refined isotropically and then by anisotropic refinement with full-matrix least-squares calculations based on $F^2$ using SHELXS [18]. All H atoms were positioned geometrically and allowed to ride on their respective parent atoms. The carboxyl H atoms were located from the difference map and allowed to ride on their parent atoms. All H atoms were refined isotropically. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [16]. Crystal data and structure refinement information for the compound **2** are summarized in Table 1.

**Table 1**: Crystal data and structure refinement for $[Cp^*Ru(CO)_2NH_2(CH_2)CH_3]BF_4$ (**2**)

| **$[Cp^*Ru(CO)_2NH_2(CH_2)CH_3]BF_4$ (Compound 2)** | |
|---|---|
| **Empirical formula** | $C_{14}H_{22}BF_4NO_2Ru$ |
| **Formula weight** | 424.21 |
| **Temperature** | 173(2) K |
| **Wavelength** | 0.71073 Å |
| **Crystal system** | Triclinic |
| **Space group** | P-1 |
| **Unit cell dimensions** | a = 10.5561(2) Å, α= 106.1380(10)°.<br>b = 11.3098(3) Å, β= 99.5730(10)°.<br>c = 16.0927(4) Å, γ = 105.3010(10)°. |
| **Volume** | 1719.56(7) $Å^3$ |
| **Z** | 4 |
| **Density (calculated)** | 1.639 $Mg/m^3$ |
| **Absorption coefficient** | 0.957 $mm^{-1}$ |
| **F(000)** | 856 |
| **Crystal size** | 0.46 x 0.24 x 0.12 $mm^3$ |
| **Theta range for data collection** | 1.36 to 28.42°. |

| $[Cp^*Ru(CO)_2NH_2(CH_2)CH_3]BF_4$ (Compound 2) | |
|---|---|
| **Index ranges** | -14≤h≤14, -14≤k≤15, -21≤l≤21 |
| **Reflections collected** | 44322 |
| **Independent reflections** | 8618 [R(int) = 0.0206] |
| **Completeness to theta = 28.42°** | 99.4 % |
| **Absorption correction** | Semi-empirical from equivalents |
| **Max. and min. Transmission** | 0.8939 and 0.6674 |
| **Refinement method** | Full-matrix least-squares on $F^2$ |
| **Data / restraints / parameters** | 8618 / 7 / 427 |
| **Goodness-of-fit on $F^2$** | 1.025 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0165, wR2 = 0.0415 |
| **R indices (all data)** | R1 = 0.0193, wR2 = 0.0437 |
| **Largest diff. peak and hole** | 0.469 and -0.487 e.Å$^{-3}$ |

## 3. Results and discussion

### *3.1 Synthesis and characterization of the $[Cp^*Ru(CO)_2NH_2(CH_2)_nCH_3]BF_4$ (1 – 5)*

The reaction of the complex $Cp^*Ru(CO)_2I$ with $AgBF_4$ in methylene chloride affords the solvated Lewis acid, $[Cp^*Ru(CO)_2]BF_4$, which reacts, in situ, with 1-alkylamines in methylene chloride at room temperature to give a pale yellow solution, from which the 1-alkylamine complex salts, $[Cp^*Ru(CO)_2NH_2(CH_2)_nCH_3]BF_4$ (**1** – **5**), were obtained. The isolated yield of the complexes decreased with increase in chain length for complexes **1** – **5**. The complexes are fairly stable in the solid state when kept at room temperature, but gradually decompose on exposure to light to give a black solid.

The complexes are soluble in chlorinated solvents and polar solvents, but are insoluble in hexane and diethyl ether. They were, therefore, easily precipitated from methylene chloride/diethyl ether mixtures. The complexes were soluble in water but their stability in water lasted for 1 h. This was established when a 1H NMR of the complexes in oxygen-free $D_2O$ was obtained but a clean $^{13}C$ NMR could not be obtained after 1 h of dissolving the solid. The high solubility in water can be attributed to the polarity of the amine group and the ionic nature of the $\eta^5$-pentamethylcyclopentadienyldicarbonyl-ruthenium(II) 1-alkylamine complex salts.

The melting point of the complexes generally decreases with increase in 1-alkylamine hydrocarbon chain length. This can be attributed to decrease in the strengths of intermolecular forces, particularly, the ionic bonds in the crystal lattice. The melting point of the complex salts with odd numbers of carbon atoms in the 1-alkanamine chain have relatively higher melting points compared to those with an even number, a trend also observed for the analogous $\eta^5$-cyclopentdienyldicarbonylruthenium(II) 1-alkylamine complexes [12]. This is probably because the complexes with the odd numbered alkanes pack better than the even numbered ones. The melting points of the complexes are higher than for their analogous Cp ruthenium complexes [12], mainly because the Cp* ligand imparts electronic and steric effects that probably increases the strength of the intermolecular interaction.

The complex salts were characterized by IR and NMR spectroscopy. The IR spectra of the complex salts **1** – **5** showed two strong absorption bands in the regions 2034 – 2029 $cm^{-1}$ and 1980 – 1994 $cm^{-1}$ assignable to νCO anti-symmetric and symmetric stretching modes, respectively. The carbonyl absorption bands for the complex salts are at lower wavenumbers than those for the analogous Cp ruthenium complexes [12]. The ruthenium centres in the Cp* complexes have higher electron density leading to increased back-bonding to the carbonyl carbon and hence weakening of C = O bond. Noteworthy, the νCO absorption bands are at higher wavenumbers in the Cp* ruthenium complex salts than the corresponding iron analogues [10]. This may be due to greater back-donation from the iron centre to the carbonyl group, than there is from the ruthenium centre to the carbonyl, thus weakening the CO bond in the iron complex. Medium absorption bands were also observed in the regions 3324 – 3309 $cm^{-1}$ and 3282 – 3271 $cm^{-1}$ assignable to ν(N–H) anti-symmetric and symmetric stretching modes respectively and a peak, observed at ca. 1600 $cm^{-1}$, is assignable to ν(N–H) bending modes. The ν(N–H) stretching bands for the complex salts are at lower wavenumbers compared to the uncoordinated ligands, due to charge transfer towards the metal centre from the coordinated nitrogen of the 1-alkylamine. This clearly indicates that the 1-alkylamine ligands are coordinated to the ruthenium centre through the nitrogen.

The $^1H$ NMR data for the complexes were obtained in $CDCl_3$ and $D_2O$. Peak assignments were done with the help of $^1H$ HSQC, as well as by comparison with data reported for analogous Cp ruthenium complexes [12]. Each of the complexes exhibited a sharp peak at ca 1.95 ppm assignable to the 15 $CH_3$ protons on the Cp* moiety. A triplet was observed at ca. 2.63, 1.22 and 0.87 ppm in the $^1H$ NMR spectra of complexes, **1**, **2** and **3**–**5** respectively, assignable to the 1-alkylamine methyl group. The resonance peaks due to the $NH_2$ protons were observed at ca.

3.30 ppm, an up-field shift of about 0.55 ppm relative to the analogous Cp ruthenium complexes [12], and a downfield shift of 1.1 ppm relative to the analogous Cp* iron complexes [10]. The up-field shift in the $NH_2$ proton resonance peaks in the Cp* ruthenium complexes relative to the analogous Cp ruthenium complexes is probably due to increased electron density on the ruthenium centre leading to reduced electrophilicity and hence shielding of the $NH_2$ protons. Furthermore, the downfield shift in the proton resonance peaks observed for the Cp* ruthenium complexes relative to the analogous Cp* iron complexes could be due to the greater ability of the ruthenium centre to accept electrons than the iron centre, thus, the $NH_2$ protons are more deshielded in Cp* ruthenium complexes [10]. Noteworthy, the $NH_2$ proton resonance peaks were observed more downfield (ca. 1.1 ppm) than those for the free 1-alkylamine ligands, a result of deshielding by the metal centre, further confirming the coordination of the 1-alkanamine ligand to the metal centre via the nitrogen atom of the $NH_2$ functionality. Peaks assignable to the CO, Cp* ring carbon atoms and $CH_3$ carbons of the Cp* in all the complexes were observed at ca. 198, 100 and 10 ppm in the $^{13}C$ NMR spectra, respectively. The CO peak for the Cp* ruthenium complexes is more up-field than for iron, while the peaks for the Cp* ring carbons and $CH_3$ carbons of the Cp* in the ruthenium complex are more downfield than in the analogous Cp* iron complexes. The $^{13}C$ NMR peaks for the methylene groups showed a significant downfield shift trend from $\alpha CH_2$ to $\omega CH_2$, a result of probable charge transfer by the methyl group towards the amine group and more so on coordination to the ruthenium metal centre.

### *3.2 Structural elucidation of complex $[Cp^*Ru(CO)_2NH_2CH_2CH_3]BF_4$*

Single crystal X-ray diffraction was used to determine the molecular structure of the complex **2**. The compound crystallized as white needle-like crystals in a triclinic crystal system, space group P-1, with two molecules, A and B, of the cation $[Cp^*Ru(CO)_2NH_2CH_2CH_3]^+$ and two counter anions $BF_4^-$ in the unit cell. This observation is contrary to that made for the analogous Cp ruthenium complex, $[CpRu(CO)_2NH_2CH_2CH_3]$, which crystallized in an orthorhombic crystal system with one cationic molecule and one counter anion in the asymmetric unit cell [12]. Fig. 1 provides the molecular diagram of the complex **2**, while Table 2 gives a comparison of important bond distances and angles.

The coordination in the cationic species of the complex **2** is in such a way that the ruthenium centre is coordinated to the 1-alkylamine ligand through a sigma bond to the amine N atom and two carbonyl ligands, forming a base, and by the $\eta^5$-cyclopentadienyl ring in the apex, giving a

pseudo-octahedral "three-legged piano stool" geometry (Fig. 1). The complex **2** adopts the energetically favoured gauche conformation, similar to that observed in other metal complexes with the Cp* ligand [10,20-22], in which the α-carbon of the 1-alkylamine lies in conformation between the cyclopentadienyl ring and the two carbonyl ligands. This confirms that the symmetric and anti-symmetric stretches, as observed in the IR data for the complex at 1980 and 2034 $cm^{-1}$, respectively, are indeed of the two nominally cis-CO ligands.

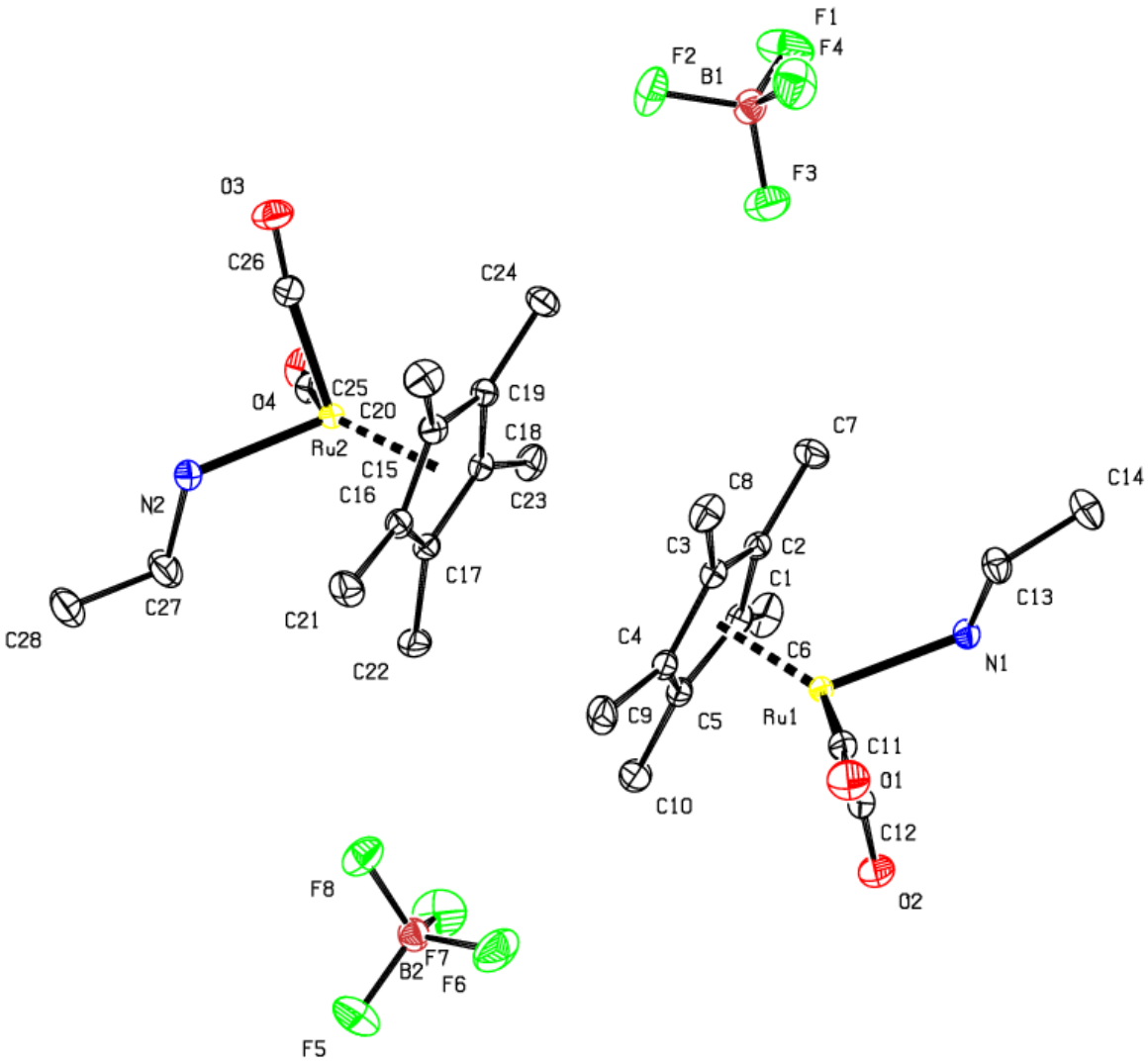


**Figure 1:** The molecular structure of compound **2** showing the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level and H atoms have been omitted for clarity

The Ru−N bond length in molecule A (2.152(10) Å) is slightly shorter than that in molecule B (2.161(10) Å), but both are longer than that reported for the analogous Cp ruthenium complex (2.139(1) Å) and Cp* iron complexes (2.022(15) Å). The slightly longer Ru−N bond observed in Cp* ruthenium complex compared to the Cp ruthenium complex can be attributed to increased electron density around the Ru metal centre leading to reduced electrophilicity and hence, weaker Ru−N bond. The C−N bond lengths for molecules A and B of the complex **2** are within the same range as that reported for the analogous Cp ruthenium complex, implying that the change from Cp to Cp* has no effect on the Ru−N bond length, contrary to the observation made in the iron complexes [10]. Noteworthy, the C=O bond length for the complex **2** is greater than that reported for the analogous Cp ruthenium complex (1.134 Å), mainly because the Cp* ring increases electron density on the metal centre, which in turn increases back-donation to the carbonyl carbon thus weakening the C=O bond as discussed earlier for the IR spectra. The bond angles in the structure of complex **2** are essentially similar to those of the analogous Cp ruthenium complexes, except for the Ru−N−C angle which is slightly greater than that reported for the analogous Cp ruthenium complex (90.35°). This difference is likely due to the steric bulk of the Cp* ring.

The coordinated 1-ethylamine has a planar conformation in the two cationic molecules in the unit cell, but the two cations are oriented in opposite directions with torsion angles for C(14)-C(13)-N(1)-Ru(1) and C(28)-C(27)-N(2)-Ru(2) being –162.48(9)° and 173.18(10)° respectively. The angles of torsion (Table 2) of the two cationic molecules imply opposite orientation in space. The crystal packing in the structure of complex **2** is such that the cationic molecules are arranged in diagonal layers with Cp* rings or alkyl chain tails of neighbouring cationic molecules, within the same layer, facing each other ( Fig. 2).

The crystal structure of the complex **2** features fairly strong N−H···F and C−H···F hydrogen bonds (Table 3). Other weak intermolecular interactions exist between C=O···C=O, O−C···F, C=O···O and C−H···O as illustrated in Figure 3.

**Table 2:** Selected bond distances (Å) and angles (°) for complex **2**

| | **Molecule A** | **Molecule B** |
|---|---|---|
| ***Cg - Ru** | 1.873 | 1.875 |
| **C(11)−O(1)** | 1.1388(16) | 1.1389(15) |
| **C(12)−O(2)** | 1.1365(16) | 1.1368(16) |

| | Molecule A | Molecule B |
|---|---|---|
| **C(13)−N(1)** | 1.4893(16) | 1.4769(17) |
| **C(13)−C(14)** | 1.5148(18) | 1.5051(19) |
| **Ru(1)−N(1)** | 2.1520(10) | 2.1612(10) |
| | | |
| ***Cg−Ru−N** | 124.66 | 124.84 |
| **N(1)−C(13)−C(14)** | 111.99(11) | 113.28(12) |
| **C(12)−Ru(1)−C(11)** | 92.89(6) | 91.93(5) |
| **C(12)−Ru(1)−N(1)** | 90.35(5) | 91.72(4) |
| **C(11)−Ru(1)−N(1)** | 91.57(5) | 91.40(5 |
| **C(13)−N(1)−Ru(1)** | 117.75(7) | 118.62(8) |
| | | |
| ***Cg−Ru−N−C13** | 76.11 | -65.67 |
| **O(2)−C(12)−Ru(1)−N(1)** | -150.2(10) | -173.6(11) |
| **O(1)−C(11)−Ru(1)−N(1)** | 162.5(14) | 156.6(9) |
| **C(14)−C(13)−N(1)−Ru(1)** | -162.48(9) | 173.18(10) |
| **C(12)−Ru(1)−N(1)−C(13)** | -152.90(9) | 162.84(11) |
| **C(11)−Ru(1)−N(1)−C(13)** | -60.00(9) | 70.87(11) |

*Cg is the centroid for C1-C5 of the Cp ring

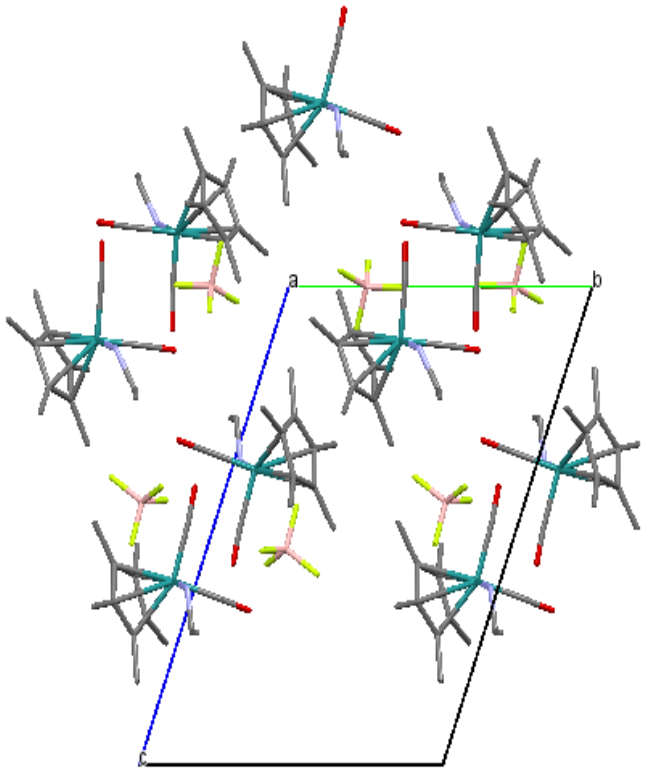


**Figure 2:** Packing diagram for $[Cp^*(CO)_2Ru\{NH_2CH_2CH3\}]BF_4$ **2** viewed along the a-axis with hydrogen atoms omitted for clarity

**Table 3:** Important intermolecular interactions and symmetry codes of the crystal structure of complex **2**

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) | |
|---|---|---|---|---|---|
| **N(1)−H(1A)···F(6)** | 0.92 | 2.13 | 2.9638(15) | 150 | 1-x,1-y,-z |
| **N(1)−H(1B)···F(8)** | 0.92 | 2.11 | 3.0196(15) | 170 | -1+x,y,z |
| **N(2)−H(2A)···F(3)** | 0.92 | 2.24 | 3.1521(15) | 169 | 1+x,y,z |
| **N(2)−H(2B)···F(2)** | 0.92 | 2.16 | 2.9801(16) | 148 | 1-x,-y,1-z |
| **C(21)−H(21A)···F(4)** | 0.98 | 2.55 | 3.4191(19) | 148 | 1-x,1-y,1-z |
| **C(21)−H(21C)···F(3)** | 0.98 | 2.48 | 3.4338(18) | 163 | 1+x,y,z |

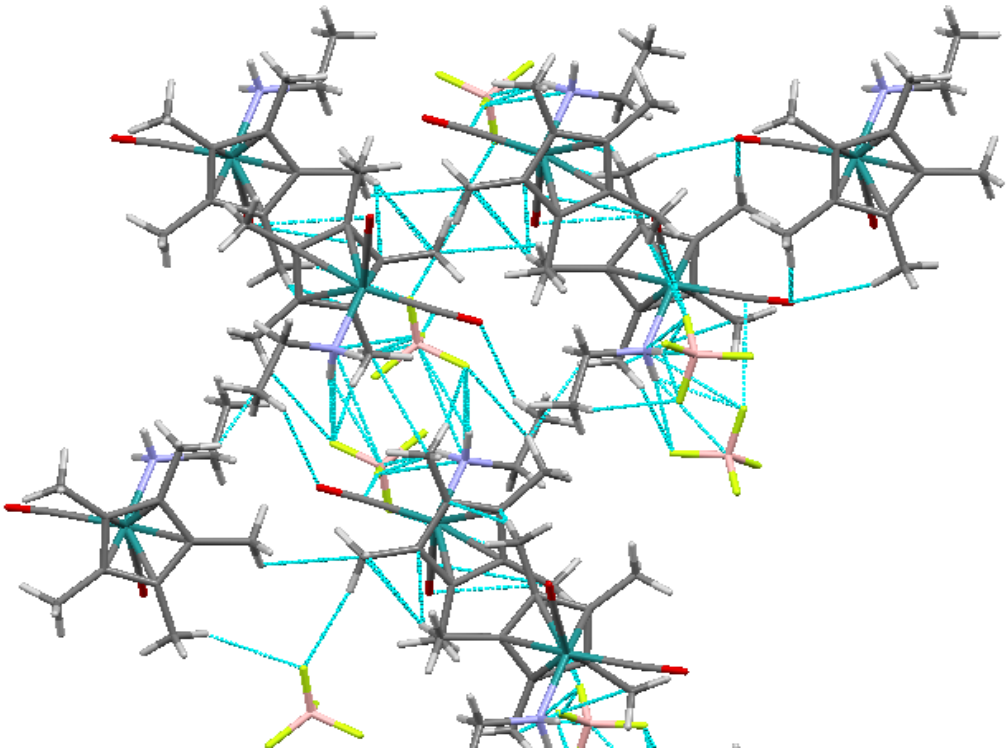

**Figure 3:** The intermolecular interactions in the molecular structure of complex **2** are indicated by the blue dotted lines

## *4. Conclusion*

The reaction of the Lewis acid $[\eta^5\text{-}C_5(CH_3)_5M(CO)_2]^+$ with 1-alkyl amines readily gave the water-soluble ruthenium complexes $[\eta^5\text{-}C_5(CH_3)_5M(CO)_2NH_2(CH_2)_nCH_3]BF_4$ (n = 0 – 4) at room temperature. Spectral data analysis has shown that the amines coordinate to the metal centre by utilizing the lone pair of electrons on the nitrogen atom. The crystal structure elucidation has shown that the stability of the complex salts can be attributed to the existence of strong intermolecular attractions, N–H···F and C–H···F, and the gauche conformation exhibited by the complex cations in the crystal. The Cp* complexes are more thermally stable than their analogous Cp molecules.

**Acknowledgements**

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# CHAPTER FIVE

## Synthesis and characterization of new α,α´-diaminoalkane-bridged dicarbonyl($\eta^5$-cyclopentadienyl)ruthenium(II) complex salts: Antibacterial activity tests of $\eta^5$-cyclopentadienyldicarbonylruthenium(II) amine complexes

Eunice A. Nyawade[a], Holger B. Friedrich[a*], Bernard Omondi[a] and Hafizah Y. Chenia[b]
*Corresponding author

[a]School of Chemistry and Physics and [b]School of Life Sciences, University of KwaZulu-Natal, Private Bag X54001, Durban 4000, South Africa

**Abstract**

Bacterial resistance to antimicrobial drugs is a significant threat to humans and requires urgent intervention. There is, therefore, a clear need for the development of new types of antibacterial agents. We have thus synthesized the α,α´-diaminoalkane-bridged diruthenium complex salts $[Rp_2NH_2(CH_2)_nNH_2]Y_2$ (Rp = $CpRu(CO)_2$ where Cp = $\eta^5$-$C_5H_5$; n = 2, 3, 4 and 6; Y = $BF_4$ (**1**) or $SO_3CF_3$(**2**)) by the reaction of $[RpNCCH_3]Y$ and $NH_2(CH_2)_nNH_2$ (n = **2** (DAE) (**3**); n = 3 (DAP) (**4**); n = 4 (DAB) (**5**) and n = 6 (DAH) (**6** $(BF)_4$, **7**$(SO_3CF_3)$) at ambient temperature and pressure. These compounds are reported for the first time and have been fully characterized by infrared spectroscopy, $^1H$ and $^{13}C$ NMR spectroscopy, elemental analyses and melting points. The crystal structures of compounds **1** and **3** were obtained by single crystal X-ray crystallography. The two compounds crystallized in the monoclinic crystal system in the $P2_1/n$ space group. Antimicrobial susceptibility tests were done for the new dinuclear complexes **3** – **7** as well as for mononuclear ruthenium complexes, $[RpBA]BF_4$ (**8**), $[RpMBA]BF_4$ (**9**), $[RpMeOBA]BF_4$ (**10**) and $[RpAMBN]BF_4$ (**11**) (BA = $NH_2CH_2C_6H_5$, MBA = $NH_2CH(CH_3)C_6H_5$, MeOBA = $NH_2CH_2C_6H_4OCH_3$ and AMBN = $NH_2CH_2C_6H_5$) against selected drug-resistant and drug-susceptible Gram-positive and Gram-negative bacteria. Some of the dinuclear and mononuclear ruthenium complexes demonstrated good potential antimicrobial activities against the bacteria tested with some showing better activity than well known antibiotics such as ampicillin (AMP 10). The ruthenium moiety $CpRu(CO)_2$ triggered or enhanced the antibacterial activity of the coordinated ligands.

Keywords: α,α′-Diaminoalkane-bridged diruthenium complexes; antimicrobial activity; Cyclopentadienyldicarbonylruthenium(II); antibacterial agents; crystal structure

## 1. Introduction

The increased rate of bacterial resistance and the need for their eradication has triggered increased interest in the development of new classes of antimicrobial agents [1], that may not be as susceptible to the bacterial mechanisms of resistance developed against the current range of drugs. Interest in the chemistry of ruthenium complexes is growing fast, due to their application in biomedicine as well as in catalysis. Ruthenium complexes containing the cyclopentadienyl group have been the subject of investigation by many research groups during the past decades because of their widespread applications in transition metal-catalyzed organic syntheses [2-10] and as anticancer agents [11-15]. The ruthenium complexes ImH[Ru(Im)(dmso)$Cl_4$] (Im=imidazole) (NAMI-A) and trans-[tetrachlorobis(1H-indazole)ruthenate(III)] (KP1019) successfully entered clinical trials as a chemotherapeutic agents, with NAMI-A showing low host toxicity at pharmacologically active doses [16-18], and KP1019 exhibiting no dose-limiting toxicity [19] and effectiveness against cancer cell lines that are highly resistant to other chemotherapeutic agents [20]. The successful use of transition metal complexes as anticancer agents [21-23] has triggered great interest in the use of metal complexes as antimicrobial agents [24-27]. Currently, a lot of research is being done on the possible application of platinum group metal complexes in medicine and more so as antibacterial agents. Palladium(II) and platinum(II) complexes have been demonstrated as potential antibacterial agents against selected bacterial strains and are more active than the free, uncoordinated ligands [28,29]. The interest in developing platinum group metal complexes as antimicrobial agents is also motivated by the fact that bacteria are rapidly developing resistance to new drugs based upon analogues of known scaffolds. Particularly, ruthenium complexes have been shown to exhibit antimicrobial activity against drug-resistant pathogenic microorganisms [30].

Dwyer and co-workers' findings, more than five decades ago, that polypyridyl mononuclear tris(bidentate)-ruthenium(II) and -iron(II) complexes, e.g. $[Ru(Me_4phen)_3]^{2+}$ ($Me_4$phen = 3,4,7,8-tetramethyl-1,10-phenanthroline), have potential antibacterial activity [31,32] inspired research into the possible use of ruthenium complexes as antimicrobial agents [33]. The activity of many organic antimicrobial and antibiotic agents has been shown to increase when directly coordinated to the ruthenium centre [34-36]. Recent studies by Li and co-workers demonstrated that the dinuclear ruthenium(II) complexes $[\{Ru(phen)_2\}_2\{Rubb_n\}]^{4+}$ {Rubbn; where phen =

1,10-phenanthroline and $bb_n$ = bis[4(4′-methyl-2,2′-bipyridyl)]-1, n-alkane} have potential antimicrobial activity against both Gram-positive *Staphylococcus aureus* and methicillin-resistant *Staphylococcus aureus* (MRSA), and Gram-negative *Escherichia coli* and *Pseudomonas aeruginosa* [37].

A majority of drugs contain at least a nitrogen atom in their structure. The $\eta^5$-cyclopentadienyldicarbonylruthenium(II) complexes reported herein are dinuclear with the ruthenium metal centers linked by α,α`-diaminoalkanes. The amine functionality-containing compounds form a very important class of therapeutic agents. A good example is 1,2-ethylenediamine, a pharmacophore of ethambutol, a front-line drug used to treat tuberculosis (TB) [38,39]. α,ω-Diaminoalkanes and bis-glycosylated diamino alcohols have been shown to exhibit good antibacterial activity against *Mycobacterium tuberculosis* [40,41]. Diethylcarbamazine (DEC) (N,N-diethyl-4-piperazine-1-carboxamide), a synthetic derivative of piperazine, and secondary amines such as N-hexylcyclohexylamine exhibited activity against filariasis causing parasites [42].

Additionally, metal carbonyls are potential CO-releasing molecules (CO-RMs); carbon monoxide delivered through organometallic CO-RMs has been shown to cause rapid death of pathogenic bacteria such as *Escherichia coli* and *Staphylococcus aureus* [43,44]. Coordinating the carbonyl ligand to the ruthenium in the complexes synthesized in this work is assumed to lead to the formation of ruthenium complexes that are active against pathogenic bacteria. Coordinating nitrogen containing ligands, such as α,α`-diaminalkanes, to a ruthenium center, such as in $\eta^5$-cyclopentadienyldicarbonylruthenium(II) moieties, thus may afford compounds with improved activity against pathogenic agents.

In our ongoing studies on the coordination of cyclopentadienyl carbonyl metal groups to various ligands [45-48], α,α′-diaminoalkane-bridged iron complexes, $[CpFe(CO)_2]_2NH_2(CH_2)_nNH_2$ [49], as well as $\eta^5$-pentamethycyclopentadienyldicarbonyliron(II) complexes, $[Fp^*_2NH_2(CH_2)_nNH_2]^{2+}$ (Fp* = $Cp^*Fe(CO)_2$ and Cp* = $C_5(CH_3)_5$) [50], in which there are no metal-metal bonds, were reported. Our success in the synthesis and characterization of the air- and water-soluble 1-alkanamine complexes of $[CpRu(CO)_2]^+$ [51] inspired us to explore the possible synthesis of α,α′-diaminoalkane complexes and study their antimicrobial activities. To the best of our knowledge, the α,α′-diaminoalkane-bridged cyclopentadienyl dicarbonyl ruthenium complex salts have not been reported previously. In this paper, we now report the

synthesis and characterization of these ruthenium complexes and their antimicrobial activities against both Gram-positive and Gram-negative bacteria.

## 2. Experimental

### *2.1 General methods and materials*

Standard Schlenk techniques were employed for all reactions using dry, distilled and nitrogen saturated solvents in all manipulations. Nitrogen gas (AFROX) was dried over phosphorus(V) oxide. Chemical reagents and solvents were obtained from the suppliers shown in parentheses: reagent grade diethyl ether (Merck) was distilled from sodium/benzophenone and stored over molecular sieves; methylene chloride (Merck) was distilled from phosphorous(V) oxide; analytical grade acetonitrile (Merck) was dried over phosphorous(V) oxide. Silver tetrafluoroborate (Merk), ruthenium trichloride hydrate (DLD, Aldrich), dicyclopentadiene (Aldrich); 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane and 1,6-diaminohexane (Aldrich), carbon monoxide (AFROX) and iodine (Unilab) were used as supplied. Melting points were recorded on an Ernst Leitz Wetzlar hot-stage microscope and are uncorrected. Elemental analyses were performed on a Thermo-Scientific Flash 2000 CHNS/O analyser. Solid state infrared spectra were recorded using an FTIR Perkin Elmer Spectrum 100 spectrophotometer between 4000 and 400 $cm^{-1}$. NMR spectra were recorded on Bruker Topspin 400 and 600 MHz spectrometers. The deuterated solvents $CDCl_3$ (Aldrich, 99.8%), $CD_3CN$ (Merck) and $D_2O$ (Aldrich) were used as purchased. Solutions for NMR spectroscopy were prepared under nitrogen using nitrogen-saturated solvents. DSC curves were recorded on a SDT Q600 V20.9 Build 20 instrument using nitrogen at a flow rate of 10 $min^{-1}$ and a temperature ramp of 5 °C $min^{-1}$. The high resolution mass spectrum for compound **10** was recorded on a Waters Synapt G2 instrument by injecting via the ESI probe into a stream of methanol. The precursors $Ru_3(CO)_{12}$ [52], $Rp_2$ (Rp = $CpRu(CO)_2$) [53], RpI [54], $[Rp]BF_4$ [55,56], as well as compounds $[RpBA]BF_4$ (**8**), $[RpMBA]BF_4$ (**9**), $[RpMeOBA]BF_4$ (**10**) and $[RpAMBN]BF_4$ (**11**) (BA = $NH_2CH_2C_6H_5$, MBA = $NH_2CH(CH_3)C_6H_5$, MeOBA = $NH_2CH_2C_6H_4OCH_3$ and AMBN = $NH_2CH_2C_6H_5$) [57] were prepared by literature methods.

### *2.2 Preparation of [RpNCCH$_3$]BF$_4$, 1*

RpI (0.3168 g) and a magnetic stirrer bar were placed in a dry Schlenk tube wrapped in aluminium foil. Silver tetrafluorborate (0.26 g) was added to the Schlenk tube and the mixture evacuated at reduced pressure for 3 h to remove any traces of moisture. Methylene chloride (20 mL) was added and the mixture stirred for 1½ h. A white precipitate and orange mother liquor were formed. The mixture was canula-filtered. Acetonitrile (5 mL) was added to the filtrate while stirring and the mother liquor immediately turned yellow. The mixture was stirred for 12 h at room temperature. The volume of the reaction mixture was reduced to 5 mL under reduced pressure. To the resulting saturated solution, excess diethyl ether (20 mL) was added, the mixture shaken and left to stand for 2 h. A greyish-yellow solid was deposited on the sides of the Schlenk tube. The mixture was canula-filtered and the residue dried under reduced pressure. Acetonitrile (10 mL) was added to the residue and the mixture stirred for 1 h to extract **1**. The Schlenk tube was left undisturbed for 20 min after which a white precipitate settled at the bottom. The mixture was canula-filtered into a Schlenk tube and the volume of the filtrate reduced to 5 mL to give a saturated solution. Diethyl ether (20 mL) was added and a greyish white precipitate appeared. The solid was purified by repeated dissolution in dry methylene chloride, canula-filtering under reduced pressure to remove any silver iodide residue and addition of dry diethyl ether until a white precipitate finally formed, which was dried under reduced pressure for 6 h. Yield: 0.2543 g, 89%; Melts at 111.8 – 112.6 °C. Anal. Calc. For $C_9H_8BF_4NO_2Ru$: C, 30.88; H, 2.30; N, 4.00%. Found: C, 30.16; H, 2.43; N, 4.18%. $^1$H NMR (600 MHz, $CDCl_3$): δ 5.73 (s, 5H, Cp), 2.88 (s, 3H, $CH_3$). $^{13}$C NMR (600 MHz, $CDCl_3$): δ 194.74 (CO), 131.37 (CN), 88.78 (Cp), 4.92 ($CH_2$). IR (solid state): ν(CO) 2079, 2032 cm$^{-1}$; ν(CN) 2332 cm$^{-1}$.

### *2.3 Preparation of [RpNCCH$_3$]SO$_3$CF$_3$, 2*

The procedure described in Section 1.2 was repeated for the synthesis of compound **2** using 15% excess of silver trifluoromethane sulphonate. Compound **2** was obtained in 90% yield. IR and NMR data obtained was very similar to those of **1**. Anal. Calc. For $C_{10}H_8F_3NO_5RuS$: C, 29.13; H, 1.96; N, 3.40 % Found: C, 29.76; H, 2.16; N, 3.20 %.

### *2.4 Preparation of [Rp$_2$DAE](BF$_4$)$_2$, 3*

Compound **1** (0.3145 g, 0.8961 mmol) was dissolved in methylene chloride (20 mL) at room temperature in a Schlenk tube. A solution of 1, 2-diaminoethane, DAE, (0.0269 g; 0.4481 mmol) in methylene chloride was added drop-wise to the stirring solution of **1**. A white precipitate appeared after 10 min. After 2 h of stirring, the mixture was left standing for 1 h and then filtered into a Schlenk tube. The residue was washed three times with 3 × 10 mL portions of methylene chloride, dissolved in acetonitrile and then left undisturbed for 30 min. It was filtered into a clean, dry, pre-weighed Schlenk tube and the volume of the solution reduced to 3 mL. Diethyl ether (10 mL) was added to the saturated solution and a white microcrystalline solid formed. The mixture was allowed to stand for 30 min and then canula-filtered. The residue was rinsed with 2 × 5 mL portions of dry diethyl ether and dried under reduced pressure for at least 6 h. Yield: 0.3534 g, 58%; Anal. Calc. for $C_{16}H_{18}B_2F_8N_2O_4Ru_2$: C, 29.50; H, 2.68; N, 4.13%. Found: C, 29.06; H, 2.34; N, 4.08%. $^1$H NMR (400 MHz, $CD_3CN$): δ 5.61 (s, 10H, Cp), 3.72 (s, 4H, $NH_2$), 2.68 (s, 4H, $CH_2$). $^1$H NMR (400 MHz, $D_2O$): δ 5.63 (s, 10H, Cp), 2.78 (s, 4H, $CH_2$). $^{13}$C NMR (400 MHz, $CD_3CN$): δ 195.43 (CO), 87.78 (Cp), 55.20 ($CH_2$). $^{13}$C NMR (400 MHz, $D_2O$): δ 195.72 (CO), 87.63 (Cp), 54.72 ($CH_2$). IR (solid state): ν(CO) 2058, 1996 cm$^{-1}$; ν(NH) 3319, 3278 cm$^{-1}$. Melts at 150 ˚C and then immediately decomposes.

### *2.5 Preparation of [Rp$_2$DAP](BF$_4$)$_2$, 4*

To a solution of **1** (0.2150 g, 0.6126 mmol) in methylene chloride (20 mL), 1,3-diaminopropane, DAP, (0.0227 mg, 0.3063 mmol) was added drop-wise at room temperature and stirred for 24 h. The mixture was filtered; the residue washed with 2 × 10 mL portions of methylene chloride to give a white solid. The white solid was extracted with 10 ml of acetonitrile and diethyl ether was added to the extract until a white precipitate formed. Filtration, followed by drying of the residue under reduced pressure, gave a white microcrystalline solid. Yield: 0.1700 g, 40%; Anal. Calc. for $C_{17}H_{20}B_2F_8N_2O_4Ru_2$: C, 29.50; H, 2.68; N, 4.13. Found: C, 29.06; H, 2.34; N, 4.08%. $^1$H NMR (400 MHz, $CD_3CN$): δ 5.61 (s, 10H, Cp), 3.65 (s, 4H, $NH_2$), 2.57 (m, JHH = 7.12 Hz, 4H, α$CH_2$), 1.65 (t, JHH = 7.20 Hz, 2H, β$CH_2$). $^1$H NMR (400 MHz, $D_2O$): δ 5.68 (s, 10H, Cp), 2.68 (m, JHH = 7.12 Hz, 4H, α$CH_2$), 1.74 (t, JHH = 7.20 Hz, 2H, β$CH_2$). $^{13}$C NMR (400 MHz, $CD_3CN$): δ 195.64 (CO), 87.76 (Cp), 51.40 (α C), 35.01 (β C). $^{13}$C NMR (400 MHz, $D_2O$): δ 195.93 (CO), 87.62 (Cp), 51.15 (α C), 35.12 (β C). IR (solid state): ν(CO) 2056, 1994 cm$^{-1}$; ν(NH) 3318, 3283 cm$^{-1}$. The compound turns into a black liquid at a temperature of 170 °C.

### *2.6 Preparation of [Rp$_2$DAB](BF$_4$)$_2$, 5*

To a solution of **1** (0.2831 g, 0.8066 mmol) in methylene chloride (15 mL), 1,4-diaminobutane, DAB, (0.0357 g, 0.4033 mmol) was added drop-wise at room temperature while stirring. The mixture was stirred for 12 h and then allowed to stand at room temperature overnight. The rest of the procedure was performed as described in Section 2.4 to give a white microcrystalline solid. Yield: 0.2741 g, 48%; Anal. Calc. for $C_{18}H_{22}B_2F_8N_2O_4Ru_2$: C, 30.62; H, 3.14; N, 3.97. Found: C, 30.49; H, 2.80; N, 4.04%. $^1$H NMR (400 MHz, $CD_3CN$): δ 5.60 (s, 10H, Cp), 3.66 (s, 4H, $NH_2$), 2.56 (m, 4H, α$CH_2$), 1.44 (m, 4H, β$CH_2$). $^1$H NMR (400 MHz, $D_2O$): δ 5.67 (s, 10H, Cp), 4.49 (s, 4H, $NH_2$), 2.69 (m, 4H, α$CH_2$), 1.50 (m, 4H, β$CH_2$). $^{13}$C NMR (400 MHz, $CD_3CN$): δ 195.72 (CO), 87.76 (Cp), 54.01 (α C), 28.73 (β C). $^{13}$C NMR (400 MHz, $D_2O$): δ 196.02 (d, CO), 87.63 (Cp), 53.91 (α C), 29.01 (β C). IR (solid state): ν(CO) 2060, 1994 cm$^{-1}$; ν(NH) 3307, 3281 cm$^{-1}$. Decomposes (turns into a black liquid) at temperature >179 °C.

### *2.7 Preparation of [Rp$_2$DAH](BF$_4$)$_2$, 6*

To a solution of **1** (0.2463 g, 0.7018 mmol) in 15 mL of methylene chloride, 1,6-diaminohexane, DAH, (0.0408 g, 0.4033 mmol) was added drop-wise at room temperature while stirring. The mixture was stirred for 18 h and then allowed to stand at room temperature overnight. The rest of the procedure was performed as described in Section 2.4 to give white microcrystalline solid. Yield: 0.1319 g, 43% yield. Anal. Calc. for $C_{20}H_{26}B_2F_8N_2O_4Ru_2$: C, 32.72; H, 3.57; N, 3.82. Found: C, 32.86; H, 3.12; N, 3.92%. $^1$H NMR (600 MHz, $CD_3CN$): δ 5.59 (s, 10H, Cp), 3.64 (s, 4H, $NH_2$), 2.57 (m, 4H, α$CH_2$), 1.45 (m, 4H, β$CH_2$) 1.25 (m, 4H, γ$CH_2$). $^1$H NMR (600 MHz, $D_2O$): δ 5.84 (s, 10H, Cp), 4.55 (s, 4H, $NH_2$), 2.85 (m, 4H, α$CH_2$), 1.68 (m, 4H, β$CH_2$) 1.48 (m, 4H, γ$CH_2$). $^{13}$C NMR (600 MHz, $CD_3CN$): δ 196.11 (CO), 88.09 (Cp), 54.76 (α C), 32.06 (β C), 25.50 (γ C). $^{13}$C NMR (400 MHz, $D_2O$): δ 196.07 (CO), 87.63 (Cp), 54.32 (α C), 31.80 (β C), 26.47 (γ C). IR (solid state): ν(CO) 2055, 2003 cm$^{-1}$; ν(NH) 3331, 3284 cm$^{-1}$. Decomposes at temperatures > 220 °C.

### *2.8 Preparation of [Rp$_2$DAH](SO$_3$CF$_3$)$_2$, 7*

To a solution of **2** (0.2463 g, 0.5974 mmol) in methylene chloride (15 mL), 1,6-diaminohexane, DAH, (0.0347 g, 0.2987 mmol) was added drop-wise at room temperature while stirring. The rest of the procedure was followed as described in Section 2.7. Yield: 0.1910 g, 49% yield.

Anal. Calc. for $C_{22}H_{26}F_6N_2O_{10}Ru_2S_2$: C, 30.77; H, 3.05; N, 3.26. Found: C, 30.91; H, 3.18; N, 3.37%. IR and NMR data obtained was very similar to that of **5a**. Decomposes at temperatures > 220 °C

### *2.9 X-ray crystal structure determination of compounds 1 and 3*

Crystals of compounds **1** and **3** suitable for single crystal X-ray diffraction studies were grown by the liquid diffusion method. A solution of the compound **3** in acetonitrile was layered with a fourfold volume excess of diethyl ether and allowed to stand undisturbed in the dark at approximately 22 °C for 24 h to give white crystals. White crystals of compound **1** were obtained by treating its solution in methylene chloride as described for compound **3.** Crystals of the two compounds were each selected and glued onto the tip of glass fibers separately. The crystals were then mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera. Crystal evaluation and data collection were performed on a Bruker Smart APEXII diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a diffractometer to crystal distance of 4.00 cm. The initial cell matrix was obtained from three series of scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range with the exposure time of about 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite [58]. Data collection method involved ω scans of width 0.5°. Data reduction was carried using the program SAINT+ [58]. The structure was solved by direct methods using SHELXS [59] and refined by SHELXL [58]. Non-H atoms were first refined isotropically and then by anisotropic refinement with full-matrix least-squares calculations based on $F^2$ using SHELXS [60]. All H atoms were positioned geometrically and allowed to ride on their respective parent atoms. All H atoms were refined isotropically. Crystal data and structure refinement information for compounds **1** and **3** are summarized in Table 1.

**Table 1:** Crystal data and structure refinement for compound **1** and **3**

| | **1** | **3** |
|---|---|---|
| **Empirical formula** | $C_9H_8BF_4NO_2Ru$ | $C_{16}H_{18}B_2F_8N_2O_4Ru_2$ |
| **Formula weight** | 350.04 | 678.08 |
| **Temperature** | 173(2) K | 173(2) K |
| **Wavelength** | 0.71073 Å | 0.71073 Å |
| **Crystal system** | Monoclinic | Monoclinic |

| | **1** | **3** |
|---|---|---|
| **Space group** | $P2_1/c$ | $P2_1/n$ |
| **Unit cell dimensions (Å, °)** | a = 6.8540(2) | a = 12.5336(5) |
| | b = 15.1790(5) | b = 12.9444(5) |
| | c = 11.5373(4) | c = 13.7516(5) |
| | β = 94.9170(10) | β = 93.562(2) |
| **Volume ($Å^3$)** | 1195.89(7) | 2226.75(15) |
| **Z** | 4 | 4 |
| **Density$_{calc}$($Mg/m^3$)** | 1.944 | 2.023 |
| **Absorption coefficient ($mm^{-1}$)** | 1.353 | 1.450 |
| **F(000)** | 680 | 1320 |
| **Crystal size ($mm^3$)** | 0.35 x 0.16 x 0.15 | 0.37 x 0.19 x 0.14 |
| **Theta range for data collection** | 2.22 to 27.99° | 2.13 to 25.00° |
| **Index ranges** | -7≤h≤9, -19≤k≤19, -15≤l≤14 | -14≤h≤14, -15≤k≤14, -16≤l≤16 |
| **Reflections collected** | 18373 | 28701 |
| **Independent reflections** | 2798 [R(int) = 0.0336] | 3915 [R(int) = 0.0321] |
| **Completeness to theta = 25.00°** | 97.5 % | 99.7 % |
| **Absorption correction** | Semi-empirical from equivalents | Semi-empirical from equivalents |
| **Max. and min. transmission** | 0.8228 and 0.6488 | 0.8228 and 0.6161 |
| **Refinement method** | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| **Data / restraints / parameters** | 2798 / 0 / 164 | 3915 / 0 / 307 |
| **Goodness-of-fit on $F^2$** | 1.119 | 1.026 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0264, wR2 = 0.0693 | R1 = 0.0238, wR2 = 0.0572 |
| **R indices (all data)** | R1 = 0.0290, wR2 = 0.0719 | R1 = 0.0268, wR2 = 0.0595 |
| **Largest diff. peak and hole** | 1.585 and -0.642 e.$Å^{-3}$ | 1.051 and -0.540 e.$Å^{-3}$ |

### *2.10 Evaluation of antimicrobial activity by disc diffusion assay*

The antimicrobial susceptibility to the complexes was determined using the disc diffusion method [61]. Stock solutions of the ruthenium and iron complexes (20 mg) were prepared in DMSO (1 mL). Sterile blank discs (6 mm; MAST, UK) were impregnated with 10 µL (0.2 mg) and 40 µL (0.8 mg), respectively, and allowed to dry for 1 h. Five Gram-negative (*Escherichia coli* ATCC 25922, *E. coli* ATCC 35218, *Klebsiella pneumoniae* ATCC 700603, *Pseudomonas*

*aeruginosa* ATCC 27853 and *P. aeruginosa* ATCC 35032) and six Gram-positive (*Bacillus subtilis* ATCC 6633, *Enterococcus faecalis* ATCC 51299, *Mycobacterium smegmatis* $mc^2155$, *Staphylococcus aureus* ATCC 29213, *S. aureus* ATCC 43300, and *S. saprophyticus* ATCC 35552) bacterial strains, grown overnight on TSA agar plates, were re-suspended in sterile distilled water and the turbidity of cell suspensions adjusted equivalent to that of a 0.5 McFarland standard. These were used to inoculate Mueller-Hinton (MH) agar plates by streaking swabs over the entire agar surface followed by the application of the respective complexes discs [61]. Plates were then incubated for 18 h at 37 °C. *M. smegmatis* $mc^2155$ plates were incubated for 48 h at 37 °C. Testing was done in duplicate and tetracycline (TE30) and ampicillin (AMP10) discs (Oxoid, UK) were used as standard antimicrobial agent controls, while DMSO-impregnated discs were used as negative controls. Zone diameters were determined and averaged. The following zone diameter criteria were used to assign susceptibility or resistance to compounds tested: Susceptible (S) ≥ 15 mm, Intermediate (I) = 11 – 14 mm, and Resistant (R) ≤ 10 mm. The criteria for assigning susceptibility or resistance to AMP10 was as follows: (S) ≥ 17 mm, (I) = 14 – 16 mm, (R) ≤ 13 mm, while those for TE30 were: (S) ≥ 19 mm, (I) 15 – 18 mm, (R) ≤ 14 mm [61]. The test results are summarized in Table 3.

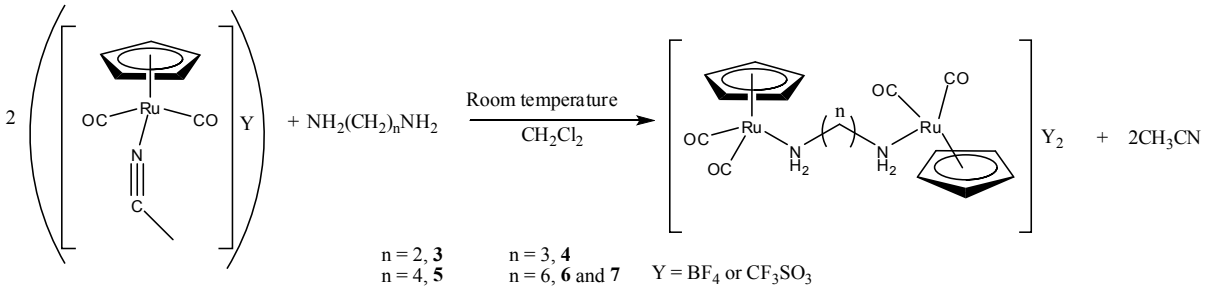
## 3. Results and Discussion

### *3.1 Synthesis and characterization of the complexes [RpNCCH$_3$]Y (1) and [Rp$_2$NH$_2$(CH$_2$)$_n$NH$_2$](Y)$_2$ (3–6 )*

The reaction of RpI (Rp = $\eta^5$-$C_5H_5Ru(CO)_2$) with a slight excess of $AgBF_4$ or $AgCF_3SO_3$ in a mixture of methylene chloride and acetonitrile took place smoothly at approximately 22 °C forming compound **1** or **2** in good yield, respectively. Although the complexes [RpNCCH$_3$]$BF_4$ and [RpNCCH$_3$]$SO_3CF_3$ are not new in the first coordination sphere [62,63], their preparation methods are new and as salts of the counter ions $BF_4^-$ and $SO_3CF_3^-$, they are reported for the first time. Compound **1** melted in a temperature range of 111.8 – 112.6 °C, compared to 140 °C reported for [RpNCCH$_3$]$PF_6$ [62].

The reaction of α,α′-diaminoalkanes with two equivalents of [RpNCCH$_3$]Y gave the new asymmetric bridged bimetallic complexes **3** – **6** in fairly good yields. The acetonitrile ligand in **1** and **2** is readily displaced by the half equivalents of the α, α′-diaminoalkanes (Scheme 1).

It is worth noting that attempts were made to synthesize the complexes **3** – **5** from the reaction of the organometallic Lewis acid $RpBF_4$ with excess α, α`-diaminoalkanes, as described for the syntheses of 1-alkanaminedicarbonyl($\eta^5$-cyclopentadienyl)ruthenium(II) tetrafluoroborate complex salts [51], but instead of the expected dinuclear complexes, a dark-brown semi-solid paste, the $^1$H NMR data of which suggested the presence of a mixture of products, was formed.




**Scheme 1:** Reaction of $[RpNCCH_3]Y$ with half equivalent of α,ω-diaminoalkanes

The complexes **3** – **6** were obtained as white microcrystalline, air-stable solids. They decompose in a temperature range of 180 °C to 225 °C. DSC-TGA curves were obtained for the compounds **2**, **5** and **6** in a temperature range of 25 °C to 500 °C. Compound **3** melts at 150 °C and begins to decompose at 180 °C, while compounds **5** and **6** do not melt but decomposes at 180 °C and 225 °C, respectively. The greatest weight change for the complexes is noted at 250 °C for all the complexes, with **3** showing the highest rate of 2.25 weight %/°C and **5** showing the lowest rate of 1.75 weight %/°C. The decomposition temperature increases with increase in the value of n. The complexes readily dissolve in water, acetonitrile, dimethyl sulphoxide and methanol, but are insoluble in non-polar solvents such as hexane, diethylether and chlorinated solvents. They also dissolve in acetone, but their stability in acetone is short-lived. The yield of the complexes decreased with increase in the value of n.

Characterization by IR, $^1$H NMR, $^{13}$C NMR and elemental analysis clearly indicated that the diamino-bridged ruthenium complexes were formed (Fig. 1). In the IR spectra, the ν(CO) absorption bands were observed as two strong peaks in the region 2060 – 2055 $cm^{-1}$ for the asymmetric CO stretching vibrations and 2003 – 1994 $cm^{-1}$ for symmetric CO stretching vibrations. The CO stretching frequencies in the α,α´-diaminoalkane complexes were observed to be at lower wavenumbers than those observed for $[RpNCCH_3]BF_4$ (2079 and 2032 $cm^{-1}$). This is consistent with the nitrogen donor atom of the amine being more electron rich than that of the acetonitrile, hence the observed shift is attributed to greater charge transfer towards the metal centre from the coordinated nitrogen of the α,α´-diaminoalkane than from the nitrogen of

acetonitrile. This shift is also a clear indication that acetonitrile is replaced by one of $NH_2$ ends of the α,α′-diaminoalkanes in the reaction. The CO stretching frequencies for the complexes **3** – **7** are lower than those reported for $[Fp_2NH_2(CH_2)_nNH_2](BF_4)_2$ [49]. This is consistent with the ruthenium centre being more electron rich than the iron centre, hence there is increased back-bonding to the carbonyl groups resulting in a lower ν(CO) absorption frequency. Two weak bands for ν(NH) were observed in the regions 3331 – 3307 $cm^{-1}$ for asymmetric NH stretching vibrations and 3284 – 3278 $cm^{-1}$ for symmetric NH stretching vibrations. The NH stretching frequencies for the coordinated α,α′-diaminoalkanes was noted to be higher than those for the starting α,α`-diaminoalkanes; an indication that they are coordinated to the Ru(II) center via the amine nitrogen. This is in agreement with the observations made for 1-alkanaminedicarbonyl($\eta^5$-cyclopentadienyl)ruthenium(II) tetrafluoroborate complex salts earlier reported [51]. A single absorption peak assignable to the C−N vibration is observed in the region 1603 – 1611 $cm^{-1}$.

The NMR data for the complexes **3** – **7** recorded in acetonitrile-$d_3$ and deuterium oxide ($D_2O$) suggests that the $CpRu(CO)_2$ units are centro-symmetrically bonded to the α,α′-diaminoalkane fragments (Fig. 1). For instance, the proton NMR data for complex **4** in acetonitrile-$d_3$ exhibited a characteristic singlet peak at ca. 5.61 ppm assignable to 10H of two identical Cp anions, a singlet at ca. 3.65 ppm for 4H on $NH_2$, a triplet at ca. 2.57 ppm assignable to the 4H of two identical α-$CH_2$ groups positioned between β-$CH_2$ and $NH_2$. A multiplet assignable to 2 protons of the β-$CH_2$ group was observed at ca. 1.65 ppm. The $^{13}C$ NMR generally gives single signals for the identical CO, α-$CH_2$, β-$CH_2$ and γ-$CH_2$ carbon atoms respectively (experimental section).

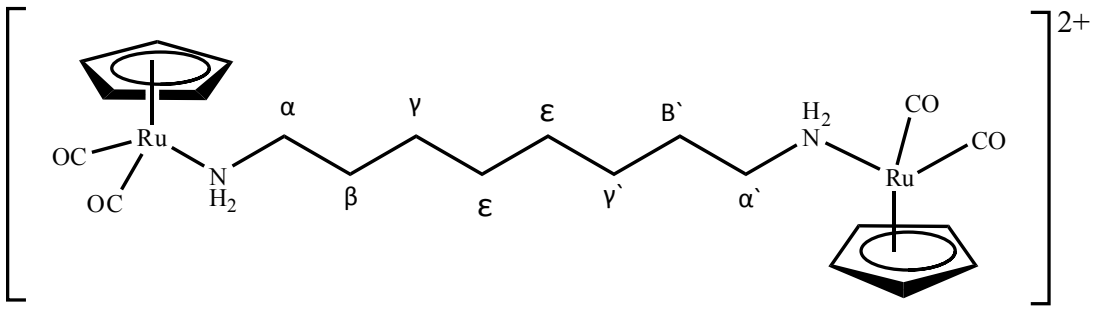



**Figure 1:** General structure of (μ - Alkane – α, α′– diamino – $\kappa^2$ N : N)bis [(dicarbonyl)($\eta^5$-cyclopentadienyl) ruthenium(II)] cation

### *3.2 Molecular structures of [Rp(CH$_3$CN)]BF$_4$ (1) and Rp$_2$NH$_2$(CH$_2$)$_2$NH$_2$][BF$_4$]$_2$ (3)*

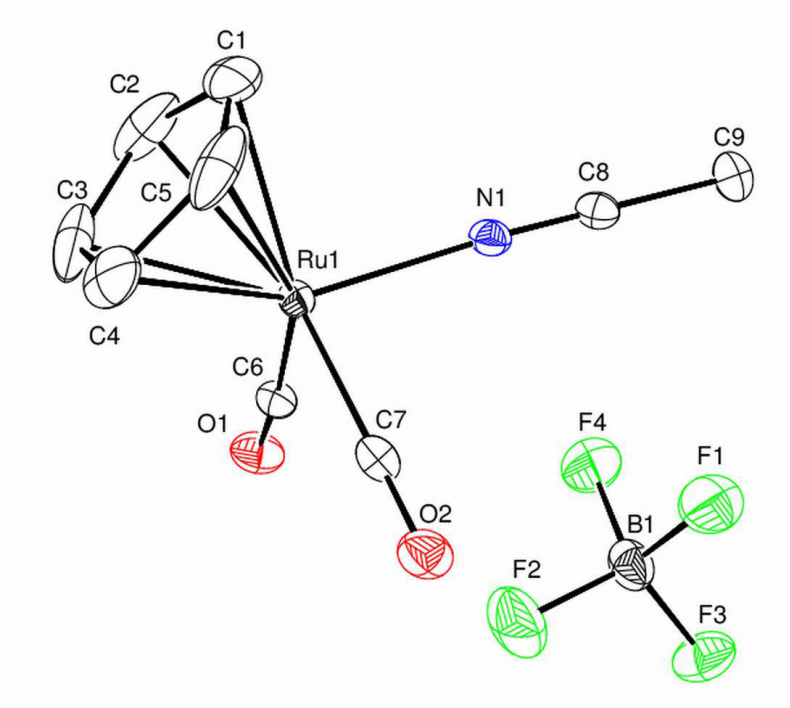



**Figure 2:** Structural view of complex **1** showing the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level and H atoms have been omitted for clarity

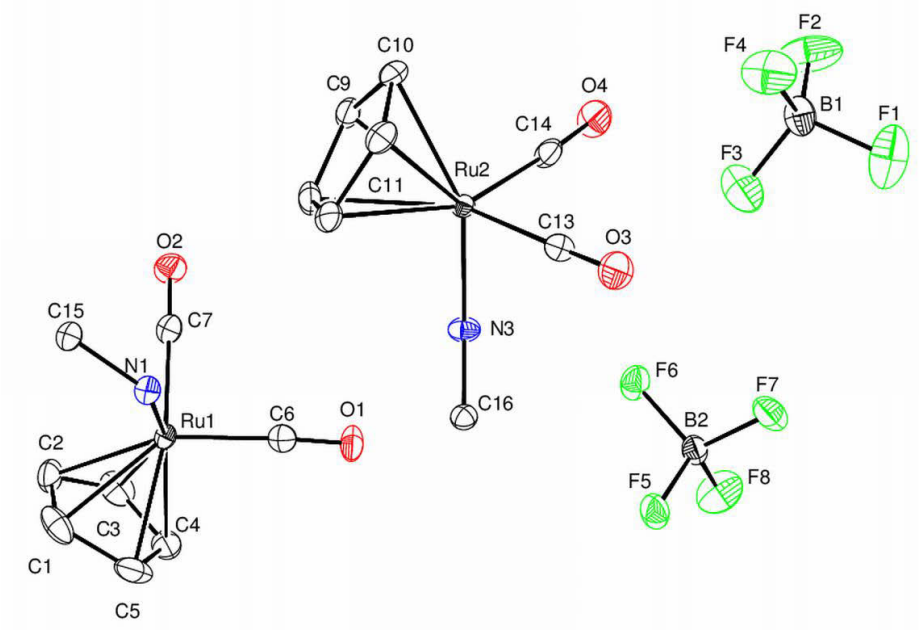



**Figure 3:** Structural view of the asymmetric unit of complex **3** showing half molecules and the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level and H atoms have been omitted for clarity

Crystals for compounds **1** and **3** were grown as described in Section 1.2 and used to obtain single crystal X-ray diffraction data. Compounds **1** and **3** crystallize as white solids in the $P2_1/n$ space group. Compound **1** crystallizes with one $[Rp(CH_3CN)]^+$ cation and one tetrafluoroborate anion (Fig 2) in the asymmetric unit. Compound **3** on the other hand crystallized with three molecules in the asymmetric unit; two half molecules of the $[Rp_2NH_2(CH_2)_2NH_2]^{+2}$ cation and two tetrafluoroborate anions (Fig 3). The other halves of the $[Rp_2NH_2(CH_2)_2NH_2]^{+2}$ cations are generated by an inversion symmetry on the C—C bond of the 1,2-diaminoethanes. Both **1** and **3** adopt a typical three-legged piano stool conformation in which the two carbonyl groups and a N atom of the acetonitrile (as in **1**) or the diamine (as in **3**) form the three legs of the stool, while the apical positions are occupied by the cyclopentadienyl ring completing the coordination around the Ru centres. The coordination around the Ru centre of **1** and **3** is similar to those reported for $[Rp(CH_3CN)]PF_6$ [62], $[RpNH_2(CH_2)_nCH_3]^+$ [51] and $[Rp_2I]^+$ [64]. The two cations in the structure of **3** are not related by symmetry. Important bond distances and angles are reported in Table 2. There are no significant differences between the bond distances and angles of **1** and those of $[Rp(CH_3CN)]PF_6$ [62].

**Table 2**: Selected inter-atomic distances (Å) and angles (°C) for complex **1** and **3**

| **Bond Parameter** | **1** | **3 (Molecule 1)** | **3 (Molecule 2)** |
|---|---|---|---|
| *Cg−Ru | 1.862(3) | 1.866 | 1.872 |
| Ru−N | 2.056(2) | 2.390(2) | 2.147(3) |
| N−C | 1.136(3) | 1.470(4) | 1.482(4) |
| *Cg−Ru−N | 124.93 | 122.25 | 125.20 |
| Ru−N−C | 176.2(2) | 116.90(2) | 115.60(2) |
| N−C−C | 179.1(3) | 110.90(2) | 111.60(2) |
| *Cg−Ru−N−C | 133.30 | 88.71 | -74.03 |
| Ru−N−C−C | 51.00(19) | -170.00(2) | 177.70(2) |
| N−C−C`−N` | - | 180.00(2) | 180.02(2) |
| Cg−Ru···Ru`−Cg` | - | 180.00 | 180.00 |

Cg is the centroid for C1-C5 of the Cp ring

Selected inter-atomic distances and angles are given in Table 2. The torsion angles Ru−N−C−C confirm that the α,`α-diaminoalkanes are σ-bonded to metal centers via the N-

atoms. The cyclopentadienyl ligands are trans to one another and the α,`α-diaminoethane ligands display a trans conformation (Fig. 4) as confirmed by the dihedral angle, Cg−Ru···Ru`−Cg = 180 ° and torsion angle, N−C−C`−N` = 180 ° respectively. There is no major difference between the Ru−Cg distances in the molecules of the two polymorphs (Cg is the centroid of the Cp rings). The bond distances are longer than those reported for $[Fp_2NH_2(CH_2)_2NH_2](BF_4)_2$ by about 0.1 Å [65]. The Ru···Ru` distance of 7.60 Å confirms that the two ruthenium atoms are not bonded to each other; comparison can be made with the non-bonded Ru···Ru` distance of 3.8 Å in $[RpCH_2Rp]$ [66] and 5.12 Å in $[RpCH_2CH_2Rp]$ [67]. The crystal structure is stabilized by N−H···F intermolecular interactions between the tetrafluoroborate anion and the cation.

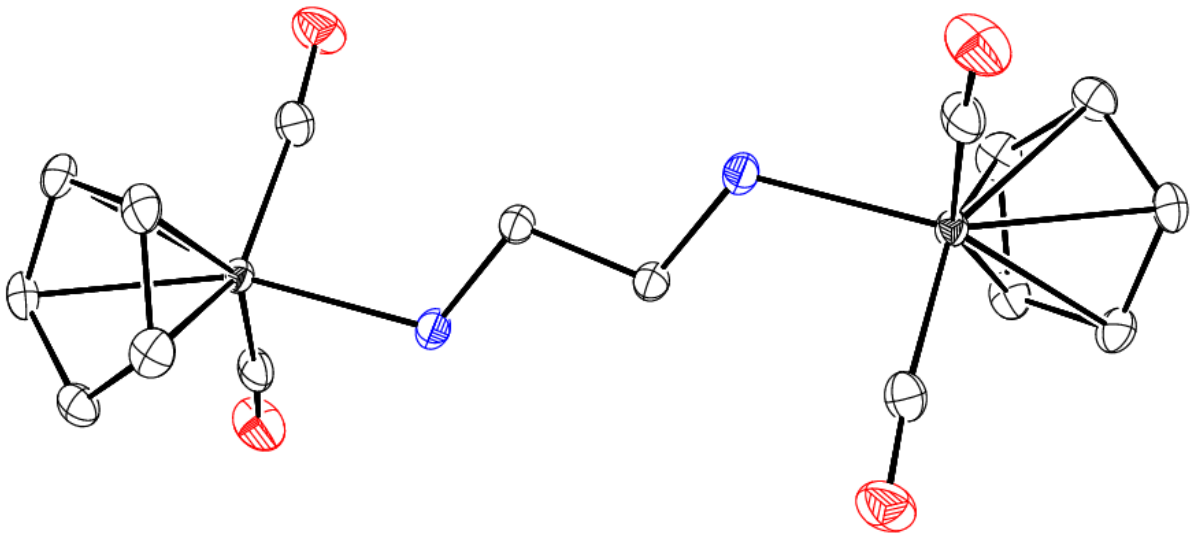


**Figure 4:** Complete structure of complex **3** showing trans conformation of Cp groups and 1,2-diaminoethane in the cation with hydrogen atoms and the counter ions omitted for clarity

### *3.3 Antimicrobial Susceptibility Tests*

Antimicrobial Susceptibility Tests (AST) were done for the dinuclear ruthenium(II) complexes **3** – **6** and the mononuclear ruthenium(II) complexes **8 - 11** against six Gram-positive and five Gram-negative bacteria (Table 3). The activity of the complexes against the bacteria was compared to those of the known antibacterial drugs, tetracycline (TE30) and ampicillin (AMP10). Of the five dinuclear ruthenium complexes tested, only complexes **3**, **5** and **6** demonstrated good antibacterial activity against some of the bacteria tested. The 1,2-diaminoethane ruthenium complex **3** showed good antimicrobial activity against methicillin-

sensitive and –resistant *S. aureus*, β-lactam-sensitive and –resistant *E. coli* and *M. smegmatis* $mc^2155$ at 20 μg/μL. The 1,6-diaminohexane complexes $[Rp_2(DAH)](BF_4)_2$ and (**6**) $[Rp_2(DAH)](SO_3CF_3)_2$ (**5**) have the same first coordination spheres and only differ by the nature of the counter ions, yet, the later demonstrated good activity against seven of the eleven bacterial strains tested (Table 3). Complex **6** demonstrated excellent antibacterial activity against *M. smegmatis* strain $mc^2155$, a bacterial strain in the same genus as the tuberculosis causing bacteria, the *M. tuberculosis*. The complex $[Rp_2(DAH)](BF_4)_2$ **(5)** only displayed good antibacterial activity against the Gram-positve *M. smegmatis* $mc^2155$ and the two Gram-negative *E. coli* strains tested. It is worth noting that the dinuclear complexes **3**, **5** and **6** are active against the ampicillin (AMP 10)- resistant Gram-negative *E.coli* ATCC 35218.

The mononuclear ruthenium complexes **9-11** demonstrated good antibacterial activity against a number of the tested bacteria, with complex **11** demonstrating very good broad spectrum activity against both Gram-negative and Gram-positive bacteria. Some of the complexes showed better activity against bacteria that are resistant to known drugs. For example, complexes **10** and **11** showed better activity against the ampicillin- and tetracycline-resistant Gram-negative *K. pneumoniae* ATTC 700603 and both strains of ampicillin-resistant *P. aeruginosa* tested. Complex **11** showed excellent antibacterial activity against the drug-sensitive *E. coli* ATTC 25922 and ampicillin-resistant *E. coli* ATTC 35218. Complexes **9** and **10** also showed excellent activity against the drug-sensitive *E. coli* ATTC 25922.

Noteworthy, the antibacterial activity of the complexes increases with increase in concentration of the complexes. Furthermore, coordination of a ligand, with the potential to be active against bacteria, to a ruthenium centre triggers antibacterial activity as demonstrated by 1,2-diaminoethane, 1,6-diaminohexane and 4-methoxybenzylamine. Even though similar observations have been documented for the antibacterial activity of some Cu(II), Co(II), Ni(II), Pd(II), and Ru(III) clomiphene complexes [68], ruthenium(II) carbonyl complexes with tridentate Schiff base [69] and palladium(II) and platinum(II) complexes with azomethines [70]; palladium(II) and platinum(II) complexes of the acetone Schiff bases of S-methyl and S-benzyldithiocarbamate are less active than the free ligand [71]. Whereas the bacteria tested in this work are resistant to these ligands, they are sensitive to ruthenium complexes of the ligands. This is clearly shown by 4-methoxybenzylamine which does not show any antibacterial activity as a ligand alone, but demonstrates broad spectrum antibacterial activity against both Gram-negative and Gram-positive bacteria when coordinated to ruthenium, as in complex **10**. This is may be because the ruthenium complexes pass through the cell wall and/or the cytoplasmic

membrane more easily, or alternatively the mechanisms by which bacteria counter the activity of antibacterial molecules are not effective against the ruthenium complexes [37,72]. This observation may also imply that many organic molecules have the potential to kill bacteria but do not have the means to enter into the bacterial cell. Thus, coordination of such a molecule, through the nitrogen of the amine, to a ruthenium centre may activate their antibacterial activity.

In general, the ruthenium complexes demonstrated antimicrobial activity against both Gram-positive and Gram-negative bacteria. According to Li et al. [37] complexes such as $[Ru(Me_4phen)_3]^{2+}$, which showed excellent activity against drug-sensitive strains were significantly less active against the corresponding current drug-resistant strains. The platinum(II) complexes of 2-acetyl pyridine thiosemicarbazone have been shown to be effective against Gram positive bacteria, but show no bactericidal effect on Gram negative bacteria [72]. Noteworthy, the compounds in the present study maintained their activity against both drug-sensitive and drug-resistant *S. aureus* and *E. coli*.

## *4. Conclusions*

The new α,α`-diaminoalkane-bridged diruthenium complex salts were successfully synthesized and characterized. The α,α`-diaminoalkanes are coordinated to two separate ruthenium metal centers via the two nitrogen donor atoms. The $CpRu(CO)_2$ units are centro-symmetrically bonded to the α,α`-diaminoalkane fragments. The crystal structure of the 1,2-diaminoalkane complex salt presents clear proof that there are no metal-metal bonds. Coordination of the diamines, α,α`-diaminoalkanes, and monoamines to ruthenium in the $CpRu(CO)_2$ moiety triggers and/or enhances their antimicrobial activity. The trifluoromethane sulfonate counter anion may have augmented the antibacterial activity of the active $[Rp_2NH_2(CH_2)_6NH_2]^{2+}$ species. The antibacterial activity is directly proportional to the concentration of the complex salt. Activity against *M. smegmatis* by the 1,2-diaminoalkane and 1,6-diaminohexane ruthenium complexes is an indication that the complexes could be active against the TB-causing bacterium, *Mycobacterium tuberculosis*. Ruthenium appears to trigger antibacterial activity in non-antibacterial organic amine molecules and also has the potential to augment the antibacterial activity of organic antimicrobial molecules.

**Table 3:** Antimicrobial susceptibility test results of the ruthenium complex compounds with zones of inhibition given to the nearest mm

| COMPOUND | GRAM-POSITIVE | | | | | | | | | | | | GRAM-NEGATIVE | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *B. subtilis* ATCC 6653 | | *E. faecalis* ATCC 51299 | | *S. aureus* ATCC 29213 | | *S. aureus* ATCC 43300 | | *S. saprophyticus* ATCC 35552 | | *M. smegmatis* $mc^2155$ | | *E. coli* ATCC 25922 | | *E. coli* ATCC 35218 | | *K. pneumoniae* ATCC 700603 | | *P. aeruginosa* ATCC 27853 | | *P. aeruginosa* ATCC 35032 | |
| | 0.2mg | 0.8 mg | 0.2 mg | 0.8 mg | 0.2 mg | 0.8 mg | 0.2 mg | 0.8 mg | 0.2 mg | 0.8 mg | 0.2 mg | 0.8 mg | 0.2 mg | 0.8 mg | 0.2 mg | 0.8 mg | 0.2 mg | 0.8 mg | 0.2 mg | 0.8 mg | 0.2 mg | 0.8 mg |
| DAE | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 8 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 10 | 0 (R) | 12 (I) | 7 (R) | 10 (R) | 0 (R) | 12 (I) | 0 (R) | 12 (I) | 0 (R) | 13 (I) |
| $[Rp_2(DAE)](BF_4)_2$ **(3)** | 0 (R) | 10 (R) | 0 (R) | 10 (R) | 9 (R) | 16 (S) | 7 (R) | 17 (S) | 0 (R) | 10 (R) | 12 (I) | 22 (S) | 0 (R) | 15 (S) | 7 (R) | 16 (S) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) |
| DAH | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 8 (R) | 8 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 13 (I) | 0 (R) | 11 (I) | 7 (R) | 12 (I) | 0 (R) | 9 (R) | 0 (R) | 9 (R) | 0 (R) | 10 (R) |
| $[Rp_2(DAP)](BF4)_2$ **(4)** | 0 (R) | 0 (R) | 9 (R) | 10 (R) | 0 (R) | 11 (I) | 8 (R) | 12 (I) | 8 (R) | 8 (R) | 0 (R) | 12 (I) | 0 (R) | 12 (I) | 0 (R) | 12 (I) | 0 (R) | 10 (R) | 0 (R) | 10 (R) | 0 (R) | 0 (R) |
| $[Rp_2(DAB)](BF_4)_2$ **(5)** | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 11 (I) | 8 (R) | 10 (R) | 8 (R) | 10 (R) | 0 (R) | 12 (I) | 0 (R) | 10 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 10 (R) | 0 (R) | 0 (R) |
| $[Rp_2(DAH)](BF4)_2$ **(6)** | 0 (R) | 0 (R) | 0 (R) | 8 (R) | 0 (R) | 10 (R) | 0 (R) | 10 (R) | 0 (R) | 10 (R) | 10 (R) | 19 (S) | 9 (R) | 15 (S) | 8 (R) | 14 (I) | 0 (R) | 0 (R) | 7 (R) | 11 (I) | 0 (R) | 11 (I) |
| $[Rp_2(DAH)]SO_3CF3$ **(7)** | 7 (R) | 19 (S) | 0 (R) | 0 (R) | 11 (I) | 18 (S) | 9 (R) | 15 (S) | 0 (R) | 12 (I) | 23 (I) | 32 (I) | 0 (R) | 16 (S) | 0 (R) | 16 (S) | 0 (R) | 15 (S) | 0 (R) | 12 (I) | 0 (R) | 0 (R) |
| [RpBA]B (**8**) | 15 (S) | 20 (S) | 0 (R) | 13 (I) | 0 (R) | 12 (I) | 0 (R) | 11 (I) | 0 (R) | 0 (R) | 0 (R) | 13 (I) | 0 (R) | 13 (I) | 0 (R) | 12 (I) | 0 (R) | 10 (R) | 0 (R) | 11 (R) | 0 (R) | 12 (I) |
| [RpMBA]B (**9**) | 10 (R) | 12 (I) | 0 (R) | 13 (I) | 0 (R) | 10 (R) | 11 (R) | 16 (S) | 0 (R) | 10 (R) | 0 (R) | 11 (I) | 0 (R) | 17 (S) | 0 (R) | 8 (R) | 0 (R) | 0 (R) | 0 (R) | 10 (R) | 0 (R) | 12 (I) |
| [RpMeOBA]B (**10**) | 0 (R) | 15 (S) | 0 (R) | 15 (S) | 0 (R) | 15 (S) | 0 (R) | 15 (S) | 0 (R) | 0 (R) | 0 (R) | 15 (S) | 8 (R) | 15 (S) | 6 (R) | 13 (I) | 0 (R) | 15 (S) | 6 (R) | 14 (I) | 7 (R) | 15 (S) |
| [RpAMBN]B (**11**) | 14 (I) | 18 (S) | 0 (R) | 13 (I) | 6 (R) | 14 (I) | 0 (R) | 14 (I) | 0 (R) | 10 (R) | 0 (R) | 10 (I) | 8 (R) | 17 (S) | 7 (R) | 16 (S) | 0 (R) | 14 (I) | 0 (R) | 14 (I) | 6 (R) | 15 (S) |
| AMBN | 0 (R) | 15 (S) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 0 (R) | 15 (S) | >30 (S) | 0 (R) | 8 (R) | 0 (R) | 12 (I) | 0 (R) | 25 (S) | 0 (R) | 20 (S) | 0 (R) | 0 (R) |
| MeOBA | 0 (R) | 11 (I) | 0 (R) | 8 (R) | 0 (R) | 10 (R) | 0 (R) | 7 (R) | 0 (R) | 0 (R) | 0 (R) | 10 (R) | 0 (R) | 9 (R) | 0 (R) | 14 (I) | 0 (R) | 10 (R) | 0 (R) | 12 | 0 (R) | 10 (R) |
| DMSO | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Tetracycline (TE30) | 36 (S) | | | | 28 (S) | | 36 (S) | | 26 (S) | | na | | 27 (S) | | 23 (S) | | 12 (R) | | 15 (I) | | 14 (R) | |
| Ampicillin (AMP10) | 40 (S) | | | | 25 (S) | | 20 (S) | | 11 (R) | | na | | 20 (S) | | 0 (R) | | 0 (R) | | 0 (R) | | 0 (R) | |

NB: Rp = $[\eta^5\text{-}C_5H_5Ru(CO)_2]$; S = Susceptible, I = Intermediate and R = resistant; DAE = 1,2-diaminoethane, DAP = 1,3-diaminopropane, DAB = 1,4-diaminobutane and DAH = 1,6-diaminohexane

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**Supplementary materials**

CCDC 1022608 and 1022609 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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# CHAPTER SIX

## Synthesis and characterization of new $\eta^5$-cyclopentadienyldicarbonylruthenium(II) amine complexes: Their application as homogeneous catalysts in styrene oxidation

Eunice A. Nyawade, Holger B. Friedrich* and Philani Mpungose
Corresponding author*

School of Chemistry and Physics, University of KwaZulu-Natal, Private Bag X54001, Durban 4000, South Africa

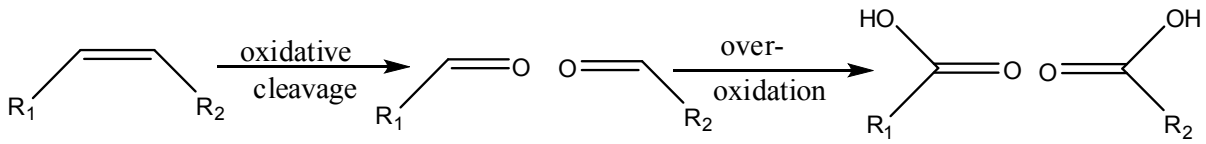
**Abstract**

The water-soluble ruthenium(II) mononuclear complexes $[CpRu(CO)_2NH_2R]BF_4$ [Cp = $\eta^5$-$C_5H_5$; R = $C_6H_{11}$ (**1**), $C_6H_5$ (**2**), $CH_2C_6H_5$ (**3**), $CH(CH_3)C_6H_5$ (**4**), $CH_2C_6H_4OCH_3$ (**5**), $CH_2C_6H_4CN$ (**6**), $C_6H_2(CH_3)_3$) (**7**), $CH_2CHCH_2$ (**8**) and $CH(CH_3)_2$ (**9**)] were synthesized from the reaction of the organometallic Lewis acid, $[CpRu(CO)_2]BF_4$, with the amine ligands at room temperature. These complexes are reported for the first time and have been fully characterized by IR, high resolution mass spectrometry, $^1H$ and $^{13}C$ NMR spectroscopy, and elemental analysis. Spectral data show that the amines are σ-bonded to the metal centre via the nitrogen atom. Crystal structures of complexes **3** and **8** were determined by single x-ray crystallography; they crystallize as white solids in the monoclinic space group $P2_1/n$. The 4-methoxybenzyl amine, 4-aminomethylbenzonitrile and allylamine preferentially bind to the metal centre via the amine nitrogen. The ruthenium complexes, **1**, **3**, **4**, **5**, **6**, **9**, $[CpRu(CO)_2NH_2CH_3]BF_4$ (**10**) and the dinuclear complex $[CpRu(CO)_2NH_2(CH_2)_6NH_2(CO)_2RuCp][BF_4]_2$ (**11**) demonstrated excellent catalytic activity in the oxidation of styrene using $NaIO_4$ as the co-oxidant with more than 95 % conversion and benzaldehyde yields respectively.

Keywords: cyclopentadienyl ruthenium, ruthenium(II) amine, styrene oxidation, ruthenium-catalysed oxidation, homogeneous catalysis.

## 1. Introduction

The development of the organometallic chemistry of ruthenium complexes is of great interest due to their multiple applications in many different scientific fields, ranging from biomedicine to catalysis [1-4]. Ruthenium complexes containing the cyclopentadienyl group have been the subject of investigation by many research groups during the past couple of decades because of their widespread applications in transition metal-catalyzed organic syntheses [5-11]. Extensive studies have been carried out on methods for specific catalytic oxidations of various organic substrates such as alcohols, amines, amides, and hydrocarbons using low-valent ruthenium complexes [12,13]. Oxidation catalysis represents the core of a variety of useful chemical processes for producing bulk and fine chemicals. One such process is the oxidation of olefins which can give a variety of products depending on the conditions of the reaction. Olefin oxidation, for example, can take place by epoxidation, dihydroxylation, vinylic and allyllic oxidation or C=C double bond cleavage (Scheme 1). The oxidative cleaveage of a C=C double bond involves cleaving the double bond with inclusion of oxygen into the two fragments forming aldehydes and/or ketones, depending on the extent of substitution. Over-oxidation of the products may result in the formation of carboxylic acids.




**Scheme 1:** General illustration of the oxidative cleavage of substituted alkenes

Oxidative cleavage of olefinic double bonds to carbonyl compounds can be achieved by ozonolysis and stoichiometric oxidation processes [14-16]. It can be effected by conversion of olefins into 1,2-diols, followed by cleavage with $NaIO_4$ or other co-oxidants [17], or by direct cleavage into a variety of functionalized products, depending on the workup conditions [18-20]. The direct oxidative cleavage of olefinic double bonds is largely achieved at industrial level by use of ozone. The large scale use of ozone for this application has major drawbacks, because of safety issues and the need to use expensive equipment [21]. There are relatively few alternative reactions that duplicate direct cleavage of olefins without formation of 1,2-diols [22,23]. Stoichiometric amounts of some transition metal compounds have been successfully used in the oxidative cleavage of olefinic double bonds. $KMnO_4$, for instance, oxidises olefins to aldehydes [24] or carboxylic acids [25-27] in water as the solvent, but the organic substrates formed are

often poorly soluble in the aqueous reaction medium. Also $KMnO_4$ cannot be used in catalytic amounts due to the irreversible precipitation of $MnO_2$ after oxidation of the substrate. On the other hand, chromyl chloride, $CrO_2Cl_2$, [28] oxidises styrene into benzaldehyde and phenylacetaldehyde [29] but its use is discouraged due to the high toxicity of chromium(VI) salts. Osmium tetroxide, $OsO_4$, has been successfully used in stoichiometric amounts and as a catalyst in the oxidation of olefins to diols and carboxylic acids, but the main drawback in its use is its high toxicity [30,31].

Simple ruthenium compounds, such as $RuCl_3.nH_2O$, $RuO_2$ and $RuO_4$, have been successfully used as catalysts for the direct oxidative cleavage of the olefinic double bonds to form aldehydes and carboxylic acids. They form a variety of reactive, high-valent oxo complexes with rich redox chemistry. $RuCl_3.\ nH_2O$, for instance, has been used as a catalyst for the oxidative cleavage of alkenes to acids [22,32,33]. To achieve the cleavages, $NaIO_4$, NaOCl or oxone ($KHSO_5$) were used as co-oxidants in different solvent systems. Most of the oxidative cleavage reactions of the olefinic double bonds gave carboxylic acids, but for the reaction where oxone was the primary oxidant with $NaHCO_3$, benzaldehyde was formed [22]. Also, $RuO_2.2H_2O$ and 2-6 equivalents $NaIO_4$ in $CCl_4/H_2O$ were used to cleave electron poor cyclic enolic olefins (C=C bond on the β-position) to aldehydes in 35-95% yield [34].

The use of catalytic amounts of ruthenium complexes in the oxidative cleavage of olefinic double bonds improves selectivity towards the cleavage products, while preventing side reactions such as epoxidation, dihydroxylation or allylic oxidation. The co-ligand coordinated to the metal plays a major role in improving the catalytic activity, as well as selectivity of the catalyst. A few ruthenium complexes, as oxidation catalysts, have demonstrated good selectivity, leading to the formation of C=C double bond cleavage products. For example, the complex cis-$[RuCl_2(bipy)_2].2H_2O$ was reported as a good catalyst in chemoselective degradation of aromatic rings to acids, with $NaIO_4$ as the co-oxidant, and oxidative cleavage of alkenes to acids, with $IO(OH)_5$ as the co-oxidant, in a $CCl_4$-MeCN-$H_2O$ biphasic solvent system [35]. The ruthenium complex $[cis\text{-}Ru(II)(dmp)_2(H_2O)_2]^{2+}$ (dmp = 2, 9 – dimethylphenanthroline) demonstrated good catalytic activity in the oxidative cleavage of terminal alkenes to aldehydes using $H_2O_2$ as the oxidant in acetonitrile at 55 °C [36]. Even though ruthenium complexes are more efficient and selective catalysts for the oxidative cleavage of alkenes to aldehydes than ruthenium salts and oxides, little attention has been given to their catalytic activity. There is, therefore, a need to synthesize ruthenium complexes with various ligands and study their catalytic activity in the oxidation of alkenes. We, therefore, carried out the synthesis and

characterization of $\eta^5$-cyclopentadienyl iron and ruthenium carbonyl complexes with nitrogen-containing species in order to develop their chemistry and also to study their catalytic and antimicrobial activities. The synthesis and characterization of the $\eta^5$-cyclopentadienyl dicarbonyl iron and ruthenium complexes of n-alkanamines [37], α,ω-diaminoalkanes [38] and N-heterocyclic ligands (DABCO, HMTA and methyl imidazole) were reported [39,40].

We now report the synthesis of nine new water-soluble ruthenium(II) complex salts, [$\eta^5$-$C_5H_5Ru(CO)_2NH_2R$]Y (Y =$BF_4$ or $CF_3SO_3$; R = $C_6H_{11}$ (**1**), $C_6H_5$ (**2**), $CH_2C_6H_5$ (**3**), $CH(CH_3)C_6H_5$ (**4**), $CH_2C_6H_4OCH_3$ (**5**), $CH_2C_6H_4CN$ (**6**), $C_6H_2(CH_3)_3$) (**7**), $CH_2CHCH_2$ (**8**) and $CH(CH_3)_2$ (**9**)) (Fig. 1), their catalytic activity and also the catalytic activity of $[CpRu(CO)_2NH_2CH_3]BF_4$ (**10**) and $[CpRu(CO)_2NH_2(CH_2)_6NH_2(CO)_2RuCp][BF_4]_2$ (**11**) in the oxidation of styrene with $NaIO_4$. To the best of our knowledge these ruthenium complexes and their catalytic activity in the oxidation of alkenes have not been reported previously.

## 2. Experimental

### *2.1 General methods and material*

Standard Schlenk techniques were employed for all reactions. Chemical reagents and solvents were obtained from the suppliers shown in parentheses. Reagent grade $Et_2O$ (Merck) was distilled from sodium/benzophenone and stored over molecular sieves; dichloromethane (Merck) was distilled from phosphorous(V) oxide. Silver tetrafluoroborate (Alfa Aesar), ruthenium trichloride hydrate (DLD-Aldrich), dicyclopentadiene (Aldrich), cyclohexylamine, aniline, benzylamine, α-methylbenzylamine, 4-methoxybenzylamine, trimethylamine, allylamine (Merck), carbon monoxide (AFROX) and iodine (Unilab) were used as supplied. 4-Aminomethylbenzonitrile was obtained from 4-aminomethylbenzonitrile hydrochloride (Merck) by neutralization using a stoichiometric amount of aqueous sodium hydroxide. Nitrogen gas (AFROX) was dried over phosphorus(V) oxide. Melting points were recorded on a Stuart Scientific melting point apparatus SMP3 and are uncorrected. Elemental analyses were performed on a Thermo-Scientific Flash 2000 CHNS/O analyser. Solid state infrared spectra were recorded using an ATR Perkin Elmer Spectrum 100 spectrophotometer between 4000 and 400 $cm^{-1}$. NMR spectra were recorded on Bruker Topspin 400 and 600 MHz spectrometers. The deuterated solvents $CDCl_3$ (Aldrich, 99.8%), DMSO, $CD_3CN$ (Merck) and $D_2O$ (Aldrich) were used as purchased. Solutions for NMR spectroscopy were prepared under nitrogen using nitrogen-saturated solvents. The high resolution mass spectra for compounds **3**, **5** and **6** were recorded on a Waters Synapt G2 instrument by injecting via the ESI probe into a stream of

methanol. The precursors $Ru_3(CO)_{12}$ [41], $[CpRu(CO)_2]_2$ (Cp = $\eta^5$-$C_5H_5$) [42], $CpRu(CO)_2I$ [43], $[Cp(CO)_2Ru]BF_4$ [44] and $[Cp(CO)_2RuNCCH_3]BF_4$ [45] were prepared by literature methods. The complexes in this work were synthesized by a modification of the method reported for the synthesis of the $\eta^5$-cyclopentadienyldicarbonylruthenium(II) n-alkanamine complex salts [37]. The ruthenium complexes **10** and **11** used for the catalytic study in this work were synthesized by previously reported methods [37,46].

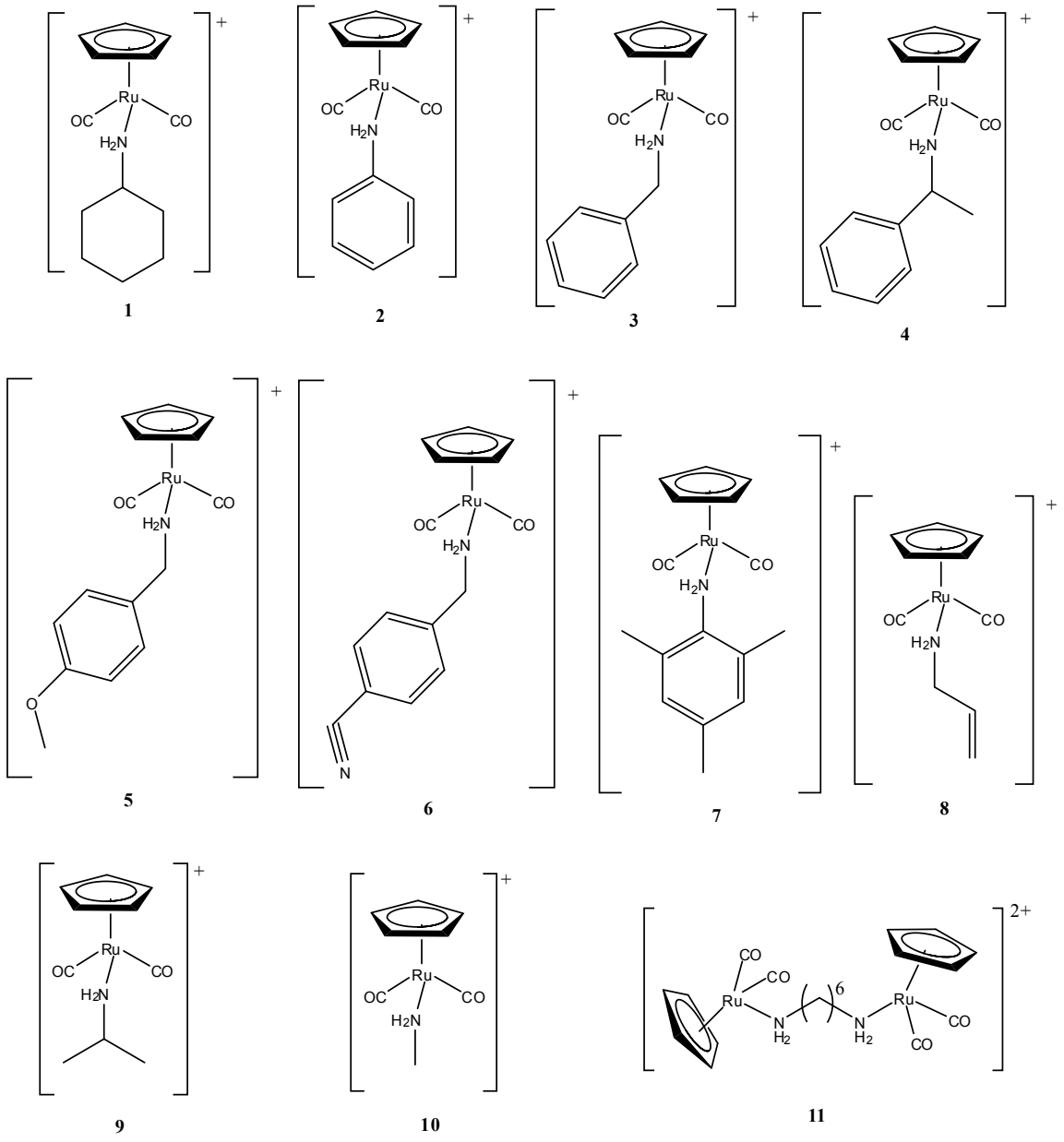



**Figure 1**: Ruthenium(II) complexes tested for catalytic activity in homogeneous oxidation of styrene

### *2.2 Synthesis of the complex salts [CpRu(CO)$_2$NH$_2$R]BF$_4$*

#### *2.2.1 Cyclohexylamine complex salt, [CpRu(CO)$_2$NH$_2$C$_6$H$_{11}$]BF$_4$, ([RpCHA]B, **1**)*

$CpRu(CO)_2I$ (0.1638 g; 0.4692 mmol), silver tetrafluoroborate (0.1261 g; 0.6478 mmol) and a magnetic stirrer bar were placed in a Schlenk tube wrapped in aluminium foil. The mixture was evacuated under reduced pressure for 3 h. Dichloromethane (DCM) (20 mL) was added and the mixture stirred for 1½ h. A white precipitate and orange mother liquor formed. The mother liquor was transferred into a clean Schlenk tube by canula filtration and a slight excess of cyclohexylamine (0.0820 g; 0.8268 mmol) added while stirring. The mother liquor immediately turned to pale yellow. The mixture was stirred for 4 h at room temperature, left to stand for ½ h and then canula-filtered under reduced pressure into a Schlenk tube. The solvent was completely removed by evaporation under reduced pressure leaving a greyish white solid. Acetonitrile (2 mL) was added to the solid to extract the complex salt. The solution was left to stand for ½ h and then filtered into a pre-weighed Schlenk tube. Diethyl ether (10 mL) was added, the mixture shaken and left to stand for 2 h. A white flaky precipitate formed, the mother liquor was filtered and the precipitate dried under reduced pressure. Yield: 0.1428 g, 74%; Melts at 188.8-189.2 °C. Anal. Found (calculated) for $C_{13}H_{18}BF_4NO_2Ru$; C, 38.15 (38.25); H, 4.52 (4.45); N, 3.39 (3.43)%. IR (solid state): $\nu_{max}/cm^{-1}$ 2056 and 1999 (CO); 2953 and 2917 ($CH_3$); 3295 and 3264 ($NH_2$). $^1$H NMR (400 MHz, $CDCl_3$): δ 5.60 (s, 5H, Cp), 3.70 (s, 2H, $NH_2$), 2.00 (m, 1H, C-1), 1.76 (m, 2H, C-2,6), 1.59 (m, 2H, C-2,6; 2H C-4), 1.23 (m, 4H, C-3,5). $^{13}$H NMR (400 MHz, $CDCl_3$): δ 195.94 (CO), 87.94 Cp), 59.90 (C-1), 33.71 (C-2,6), 24.59 (C-4), 24.23 (C-3,5).

#### *2.2.2 Phenylamine complex salt, [CpRu(CO)$_2$NH$_2$C$_6$H$_5$]BF$_4$, ([RpPhA]B, **2**)*

$CpRu(CO)_2I$ (0.1240 g; 0.3552 mmol) and a slight excess of silver tetrafluoroborate (0.0892 g; 0.4582 mmol) were dried, dissolved in DCM (15 mL) and treated as described in Section 2.2.1. Excess of phenylamine (0.0621 g; 0.6668 mmol) was added to the filtrate obtained and the mixture stirred for 8 h at room temperature. The rest of the procedure was performed as described in Section 2.2.1 to give a white solid. Yield: 0.0845 g, 58%; Melts at 116.8-117.6 °C. Anal. Found (calculated) for $C_{13}H_{12}BF_4NO_2Ru$; C, 37.92 (38.83); H, 3.16 (3.01); N, 3.51 (3.48)%. IR (solid state): $\nu_{max}/cm^{-1}$ 2050 and 1992 (CO); 3310 and 3274 ($NH_2$). $^1$H NMR: (400 MHz, $CD_3CN$) δ 7.53-7.37 (m, 5H, $C_6H_5$), 5.68 (s, 5H, Cp), 4.41 (s, 2H, $NH_2$). $^{13}$C NMR: (400 MHz, $CD_3CN$) δ 195.83 (CO), 128.44-128.04 (C- $C_6H_5$), 87.57 (Cp).

### *2.2.3 Benzylamine complex salt, $[CpRu(CO)_2NH_2CH_2C_6H_5]BF_4$, ([RpBA]B, **3**)*

$CpRu(CO)_2I$ (0.1760 g; 0.5042 mmol) and $AgBF_4$ (0.1276 g; 0.6555 mmol) were placed in a Schlenk tube wrapped with aluminium foil and treated as described in Section 2.2.1. Excess benzylamine (0.0992 g; 0.9265 mmol) were added to the resulting orange filtrate and the mixture treated as described in Section 2.2.2 above to give a white solid. Yield: 0.0928 g, 44%; Melts at 136.7-137.6 °C. Anal. Found (calculated) for $C_{14}H_{14}BF_4NO_2Ru$; C, 40.37 (40.41); H, 3.34 (3.31); N, 3.35 (3.37)%. $M^+$, 330.007 (330.0068). IR (solid state): $\nu_{max}/cm^{-1}$ 2052 and 1986 (CO); 3325 and 3286 ($NH_2$). $^1H$ NMR: (400 MHz, $CD_3CN$) δ 7.41-7.33 (m, 5H, $C_6H_5$), 5.60 (s, 5H, Cp), 4.04 (s, 2H, $NH_2$), 3.78 (t, 2H, $CH_2$). $^{13}C$ NMR: (400 MHz, $CD_3CN$) δ 195.57 (CO), 138.27 ($\underline{C}$-$CH_2$), 128.57-128.12 ($C_6H_5$), 87.73 (Cp), 57.27 ($CH_2$).

### *2.2.4 (±)-α-Methylbenzylamine complex salt, $[CpRu(CO)_2NH_2(CH)CH_3C_6H_5]BF_4$ ([RpMBA]B, **4**)*

$CpRu(CO)_2I$ (0.0953 g; 0.2730 mmol) and a slight excess of $AgBF_4$ (0.0701 g; 0.3601 mmol) were placed in a Schlenk tube wrapped with aluminium foil and treated as described in Section 2.2.1. Excess **(±)**-α-methylbenzylamine (0.0658 g; 0.5430 mmol) was added to the resulting orange solution and the mixture treated as described in Section 2.2.2 above to give a white solid. Yield: 0.0673 g, 57%; Melts at 170.1-170.7 °C. Anal. Found (calculated) for $C_{15}H_{16}BF_4NO_2Ru$; C, 41.79 (41.88); H, 3.78 (3.75); N, 3.25 (3.26)%. IR (solid state): $\nu_{max}/cm^{-1}$ 2054 and 1995 (CO); 3301and 3266 ($NH_2$). $^1H$ NMR: (400 MHz, $CD_3CN$) δ 7.45-7.33 (m, 5H, $C_6H_5$), 5.45 (s, 5H, Cp), 4.28(s, 1H, $NH_2$), 4.01 (s, 1H, $NH_2$), 3.66 (m, 1H, CH), 1.49 (d, 3H, $CH_3$). $^{13}C$ NMR: (400 MHz, $CD_3CN$) δ 195.66 (CO), 195.59 (CO), 141.99 ($\underline{C}$-CH), 128.74 (C-ortho), 127.03 (C-para), 129.14 (C-meta), 87.97 (Cp), 87.95 (Cp), 61.91 ($CH_2$), 23.99 ($CH_3$).

### *2.2.5 4-Methoxybenzylamine complex salt, $[CpRu(CO)_2NH_2CH_2(C_6H_4)OCH_3]BF_4$ ([RpMeOBA]B, **5**)*

$CpRu(CO)_2I$ (0.0700 g; 0.2005 mmol) and a slight excess of $AgBF_4$ (0.04893 g; 0.2513 mmol) were placed in a Schlenk tube wrapped with aluminium foil and treated as described in Section 2.2.1. Excess 4-methoxybenzylamine (0.1213 g; 0.8842 mmol) was added to the resulting orange filtrate and stirred for 6 h. The resulting pale yellow solution was treated as described in Section 2.2.2 to give a white solid. Yield: 0.0508 g, 57%; Melts at 174.9-175.6 °C. Anal. Found (calculated) for $C_{15}H_{16}BF_4NO_2Ru$; C, 40.37 (40.38); H, 3.59 (3.61); N, 3.13 (3.14)%. HRMS:

$M^+$ 360.0172 (360.0174). IR (solid state): $\nu_{max}/cm^{-1}$ 2053, 2001 and 1974 (CO), 3306 and 3271 ($NH_2$). $^1H$ NMR: (400 MHz, $CDCl_3$) δ 5.44 (s, 5H, Cp), 4.22 (s, 2H, $NH_2$), 7.25 (d, 2H, =oCH ), 6.86 (d, 2H, =mCH), 3.64 (t, $J_{HH}$ = 7.04 Hz, 2H, $NCH_2$), 3.75 (s, 3H, $OCH_3$). $^{13}C$ NMR: (400 MHz, $CDCl_3$) δ 195.14 (CO), 87.84 (Cp), 130.52 (C-$CH_2$), 129.45 (oCH), 114.55 (mCH), 160.1 (C-p$OCH_3$), 56.29 (C-$NH_2$), 55.24 ($OCH_3$).

### *2.2.6 4-Aminomethylbenzonitrile complex salt, $[CpRu(CO)_2NH_2CH_2(C_6H_4)CN]BF_4$ ([RpAMBN]B, **6**)*

$CpRu(CO)_2I$ (0.160 g; 0.4583 mmol), $AgBF_4$ (0.1181 g; 0.6067 mmol) and a stirrer bar were placed in a Schlenk tube wrapped with aluminium foil and treated as described in Section 2.2.1. Excess 4-aminomethylbenzonitrile (0.1175 g; 0.8893 mmol) was dissolved in tetrahydrofuran (10 mL), added to the filtrated and the mixture stirred for 4 h. The mother liquor was filtered into a clean Schlenk tube by use of a canula. The solvent was completely removed by evaporation under reduced pressure leaving a pale yellow oil. Acetonitrile (2 mL) was added to the oil, the solution left to stand for ½ h and then filtered into a pre-weighed Schlenk tube. Diethyl ether (10 mL) was added to the filtrate, the mixture shaken and a white suspension appeared. The mixture was left undisturbed for 12 h. Shiny white crystals formed. The crystals were separated from the mother liquor and dried under reduced pressure. Yield: 0.1208 g, 59%; Melts at 177.2 – 178.0 °C. Anal. Found (calculated) for $C_{15}H_{13}BF_4N_2O_2Ru$; C, 40.82 (40.84); H, 3.01 (2.97); N, 6.28 (6.35)%. HRMS: $M^+$ 355.0024 (355.0021). IR (solid state): $\nu_{max}/cm^{-1}$ 2061 and 2006 (CO); 2229 (C8-N); 3306 and 3271 ($NH_2$). $^1H$ NMR: (400 MHz, DMSO) δ 7.90 (d, 2H, mCH), 7.59 (d, 2H, oCH), 5.81 (s, 5H, Cp), 5.37 (s, 2H, $NH_2$), 3.78 (s, 2H, $CH_2$). $^{13}C$ NMR: (400 MHz, DMSO) δ 196.64 (CO), 144.41 (C-$CH_2$), 132.41 (mCH), 129.29 (oCH), 118.64 (CN), 110.61 (C-CN), 88.60 (Cp), 56.28 (C-7).

### *2.2.7 2,4,6-Trimethylaniline complex salt, $[CpRu(CO)_2NH_2(CH_3)_3C_6H_2]BF_4$ ([RpTMA]B, **7**)*

$CpRu(CO)_2I$ (0.0728 g; 0.2085 mmol) and $AgBF_4$ (0.0598 g; 0.3072 mmol) were placed in a Schlenk tube wrapped with aluminium foil and treated as described in Section 2.2.1. Excess 2,4,6-trimethylaniline (0.0246 g; 0.4164 mmol) were added to the resulting orange filtrate and the mixture treated as described in Section 2.2.2 to give a white solid. Yield: 0.0571 g, 62%; Decomposes at temperatures above 188 °C. Anal. Found (calculated) for $C_{16}H_{18}BF_4NO_2Ru$; C, 43.24 (43.26); H, 4.05 (4.08); N, 3.17 (3.15)%. IR (solid state): $\nu_{max}/cm^{-1}$ 2049, 1987 and 1953 (CO): 3270 ($NH_2$). $^1H$ NMR: (400 MHz; $CDCl_3$) δ 6.73 (s, 2H, =CH), 5.68 (s, 5H, Cp), 5.42(s,

2H, $NH_2$), 2.29 (s, 3H, p-$CH_3$), 2.19 (s, 6H, o-$CH_3$). $^{13}$C NMR: (400 MHz, $CDCl_3$) δ 194.87 (CO), 140.98 (C-$NH_2$), 135.28 (C-p$CH_3$), 130.19 (CH), 126.63 (C-o$CH_3$), 88.08 (Cp), 20.56 (p-$CH_3$), 17.50 (o-$CH_3$).

### *2.2.8 Allylamine complex salt, $[CpRu(CO)_2NH_2CH_2CHCH_2]BF_4$ (**8**)*

To a solution of $[CpRu(CO)_2NCCH_3]BF_4$ (0.1214 g; 0.3468 mmol) in DCM (20 ml), allylamine (0.0349 g; 0.6111 mmol) was added drop wise at room temperature and stirred for 12 h. The resulting pale yellow solution was evaporated to dryness and the product extracted with acetonitrile (5 mL). The mixture was filtered and the volume of filtrate reduced to about 2 mL. Diethyl ether (10 mL) was added to the extract and a white precipitate formed. Filtration, followed by drying of the residue under reduced pressure gave a white solid. Yield: 0.0874 g, 72%. Decomposes at temperature > 120 ˚C Anal. Found (calculated) for $C_{10}H_{12}BF_4NO_2Ru$; C, 32.84 (32.81); H, 3.29 (3.30); N, 3.81 (3.83)%. IR (solid state): $\nu_{max}/cm^{-1}$ 2059, 2016 (CO): 3315, 3280 $cm^{-1}$ ($NH_2$). $^1$H NMR: (400 MHz, $CDCl_3$) δ 5.88 (m, 1H, C-β); 5.60 (s, 5H, Cp); 5.42 (d, 1$H_a$, C-γ trans); 5.27 (d, 1$H_b$, C-γ cis); 3.79 (s, 2H, $NH_2$); 3.30 (q, 2H, C-α). $^{13}$C NMR: (400 MHz; $CDCl_3$) δ 196.00 (CO); 135.17 (C-β), 118.57 (C-γ); 88.04 (Cp); 55.97 (C-α).

### *2.2.9 Isopropylamine complex salt, $[CpRu(CO)_2NH_2CH(CH_3)_2]BF_4$ ([RpiPrA]B, **9**)*

$CpRu(CO)_2I$ (0.0982 g; 0.2813 mmol) and $AgBF_4$ (0.0602 g; 0.3092 mmol) were placed in a Schlenk tube wrapped with aluminium foil and treated as described in Section 2.2.1. Excess isopropylamine (0.0325 g; 0.5498 mmol) were added to the resulting orange solution and the mixture treated as described in Section 2.2.2. A white solid was formed. Yield: 0.0792 g, 77%; Decomposes at temperatures above 188 °C. Anal. Found (calculated) for $C_{10}H_{18}BF_4NO_2Ru$; C, 32.64 (32.63); H, 3.81 (3.83); N, 3.79(3.81)%. IR (solid state): $\nu_{max}/cm^{-1}$ (CO) 2058, 2018 and 2002; 3331 and 3293 ($NH_2$). $^1$H NMR: (400 MHz, DMSO) δ 5.80 (s, 5H, Cp), 4.80 (s, 2H, $NH_2$), 2.58 (m, 1H, CH), 1.08 (d, 6H, $CH_3$). $^{13}$C NMR: (400 MHz, DMSO) δ 196.00 (CO); 88.23 (Cp), 51.89 (C-2), 23.11 ($CH_3$).

### *2.3 X-ray crystal structure determination of compounds 3 and 8*

**Table 1:** Crystal data and structure refinement for compounds **3** and **8**

| | **Compound 3** | | **Compound 8** | |
|---|---|---|---|---|
| **Identification code** | 13bo_hbf_ne6_0m | | 13ub_hbf_ne7_0m | |
| **Empirical formula** | $C_{14}H_{14}BF_4NO_2Ru$ | | $C_{10}H_{12}BF_4NO_2Ru$ | |
| **Formula weight** | 416.14 | | 366.09 | |
| **Temperature** | 173(2) K | | 173(2) K | |
| **Wavelength** | 0.71073 Å | | 0.71073 Å | |
| **Crystal system** | Monoclinic | | Monoclinic | |
| **Space group** | P21/n | | P 21/n | |
| **Unit cell dimensions (Å, °)** | a = 10.4488(3)<br>b = 9.7788(4)<br>c = 31.7901(11) | α = 90<br>β = 99.2360(10)<br>γ = 90 | a = 8.7303(3)<br>b = 9.7841(3)<br>c = 15.4342(5) | α = 90<br>β = 91.5250(10)<br>γ = 90 |
| **Volume** | 3206.10(19) $Å^3$ | | 1317.89(7) $Å^3$ | |
| **Z** | 8 | | 4 | |
| **Density (calculated)** | 1.724 $Mg/m^3$ | | 1.845 $Mg/m^3$ | |
| **Absorption coefficient** | 1.025 $mm^{-1}$ | | 1.232 $mm^{-1}$ | |
| **F(000)** | 1648 | | 720 | |
| **Crystal size** | 0.39 x 0.28 x 0.14 $mm^3$ | | 0.360 x 0.250 x 0.240 $mm^3$ | |
| **Theta range for data collection** | 1.98 to 28.45°. | | 2.465 to 28.307°. | |
| **Index ranges** | -13≤h≤14, -11≤k≤13, -42≤l≤42 | | -11≤h≤11, -12≤k<=13, -20≤l≤20 | |
| **Reflections collected** | 40725 | | 25223 | |
| **Independent reflections** | 8054 [R(int) = 0.0185] | | 3282 [R(int) = 0.0242] | |
| **Completeness to theta = 25.00°** | 99.9 % | | 100.0 % | |
| **Absorption correction** | Semi-empirical from equivalents | | Semi-empirical from equivalents | |
| **Max. and min. transmission** | 0.8698 and 0.6907 | | 0.744 and 0.698 | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | | Full-matrix least-squares on $F^2$ | |
| **Data / restraints / parameters** | 8054 / 0 / 415 | | 3282 / 0 / 180 | |
| **Goodness-of-fit on $F^2$** | 1.090 | | 1.050 | |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0238, wR2 = 0.0546 | | R1 = 0.0195, wR2 = 0.0455 | |
| **R indices (all data)** | R1 = 0.0259, wR2 = 0.0557 | | R1 = 0.0223, wR2 = 0.0475 | |
| **Largest diff. peak and hole** | 0.827 and -0.479 $e.Å^{-3}$ | | 0.850 and -0.661 $e.Å^{-3}$ | |

Crystals of compounds **3** and **8** suitable for single crystal X-ray diffraction studies were grown by the liquid diffusion method. A solution of each of the compounds **3** and **8** in acetonitrile were layered with a fourfold volume of diethyl ether and allowed to stand undisturbed in the dark at room temperature for 24 hours to give white crystals. Crystals of compounds **3** and **8** were selected and glued onto the tip of glass fibres separately. The crystals were then mounted in a stream of cold nitrogen at 100(1) K and centred in the X-ray beam using a video camera. The rest of the manipulations were done as per the literature method [47]. Crystal data and structure refinement information for compounds **3** and **8** are summarized in Table 1

### *2.4 Catalytic studies*

In a typical experiment, a known amount of the co-oxidant was placed in a dry Schlenk tube equipped with a magnetic stirrer bar under an atmosphere of nitrogen. Deionised water (3 mL) was added and the mixture stirred at a selected temperature until the co-oxidant dissolved completely (where applicable). The $\eta^5$-cyclopentadienyldicarbonylruthenium(II) amine complex and acetonitrile (3 mL) were added and the mixture stirred until all the ruthenium complex had dissolved. Styrene (0.478 mmol) and the internal standard, benzophenone (0.478 mmol), were added to the mixture in the Schlenk tube, stirred for 1 min and then sampled for gas chromatography (GC) analysis. The stirring was continued and the progress of the reaction monitored hourly by GC. The complex $[CpRu(CO)_2NH_2C_6H_{11}]BF_4$ (**1**) was used as the model catalyst for optimization of the catalytic conditions. Its catalytic activity was investigated at room temperature (22 °C), 40 °C and 60 °C; with different co-oxidants at 60 °C; with different concentrations of $NaIO_4$ at 60 °C; in different solvent systems at 60 °C using the best co-oxidant; and in different reaction media (acidic – $H_2SO_4$, basic – $K_2CO_3$ and N-methylmorpholine, or neutral). The effect of varying the catalyst concentration on conversion and yield was also investigated under the chosen conditions using 0.5, 1.5 and 2.5 mol% complex **1**. The catalytic activity of the ruthenium complexes **1**–**6** and **9** were examined and compared at the optimized conditions. The percentage yield of benzaldehyde was calculated on the basis of the GC analysis with benzophenone as the internal standard. The time taken to achieve the highest conversion and benzaldehyde yield is given for each reaction, as presented in the bar graphs in Section 3.3. Best reaction conditions chosen were 0.478 mmols styrene, 3 equiv. $NaIO_4$, $CH_3CN$:$H_2O$ (1:1; 6 mL) at 60 °C; any changed parameter is stated for each reaction. The time taken to achieve highest conversion is given in h.

## 3. Results and discussion

### *3.1 Synthesis and Characterization*

The mononuclear complexes $[CpRu(CO)_2NH_2R]BF_4$ [Cp = $\eta^5$-$C_5H_5$; R = $C_6H_{11}$ (**1**), $C_6H_5$ (**2**), $CH_2C_6H_5$ (**3**), $CH(CH_3)C_6H_5$ (**4**), $CH_2C_6H_4OCH_3$ (**5**), $CH_2C_6H_4CN$ (**6**), $C_6H_2(CH_3)_3$) (**7**), $CH_2CHCH_2$ (**8**) and $CH(CH_3)_2$ (**9**)] were formed in fairly good yield from the reaction of the organometallic Lewis acid, $[CpRu(CO)_2]BF_4$, with the respective amines at room temperature. The complexes form white, air-stable crystals which are generally soluble in polar solvents such as water, methanol, acetone, acetonitrile and dimethylsulfoxide, and in chlorinated solvents, chloroform and methylene chloride in some cases. They are insoluble in non-polar solvents, such as hexane and diethyl ether. The elemental analyses and high resolution mass spectrometry results for the complexes correlate with the calculated values; an indication that the complexes were formed as predicted.

The $^1$H NMR data for the complexes was obtained and peaks were assigned using 2D NMR, as well as $D_2O$ tests for the amine protons. The $^1$H NMR spectra for the complexes in $CDCl_3$, $CD_3CN$ and $D_2O$ showed a sharp singlet peak in the region ca. 5.60 - 5.75 ppm, assignable to the five equivalent Cp protons. This is an indication that the ligands in complexes **5**, **6** and **8**, which have two possible coordination sites, bonded to the metal centre via only one of the sites. Coordination to both sites would have shown a single peak in the same region ca. 5.60 – 5.75 ppm but assignable to 10 protons for the Cp peaks in the $^1$H NMR spectrum. Regioselective coordination of the metal to the $NH_2$ is clearly indicated by the downfield shift in the amine proton peaks, in the $^1$H NMR spectra of compounds **5**, **6** and **8**, relative to those of the uncoordinated ligands. For the complexes **1**, **8** and **9**, a singlet peak in the $^1$H NMR spectra obtained in $CDCl_3$ was observed at ca. 3.70, 3.79 and 3.78 ppm respectively, and assigned to the two amine protons. The amine proton signals in the complexes were observed more downfield than those of the free ligand peaks (approx. 2 ppm), probably due to the de-shielding by the metal centre; an indication of coordination of the amines to the metal centre through the N atom [37]. Hydrogen bonding between the amine group protons and the fluoride atoms of the tetrafluoroborate counter anion can also contribute to the downfield shift of the amine protons in the $^1$H NMR spectra. The amine proton peaks for complexes **2**, **3**, **5**, **6** and **7** were observed more downfield than in **1**, **8** and **9** due to the electron withdrawing effect of the aromatic ring. It is worth noting that, whereas the amine group proton peak for the free ligand in complex **4** was observed as singlet peak at ca. 1.59 ppm, two singlet peaks were observed at ca. 4.28 and 4.01 ppm for the complex in the $^1$H NMR spectrum in $CD_3CN$. This is an indication that the two $NH_2$

protons are diastereotopic. The reason only one NMR signal is observed for the $NH_2$ protons in the free amine is rapid inversion on the N centre, which, cannot happen when the amine is coordinated to Ru. The $^1H$ NMR spectrum of complex **8** shows well resolved characteristic olefinic peaks; a multiplet peak assignable to the single proton attached to the β-carbon atom was observed at ca. 5.88 ppm and two doublets observed at ca. 5.42 and 5.27 ppm, each integrating for 1 proton, assignable to the two non-equivalent protons, Ha and Hb respectively, on the γ-carbon atom (Fig. 2). These values are within the range reported for the analogous iron complexes [39]. The protons on the α-carbon atom exhibited a quartet at ca. 3.30 ppm, a downfield shift by 0.35 ppm from that reported for the iron complex analogue [39].

The $^{13}C$ NMR spectra of the complexes show two peaks at ca. 87.8 and 195.7 ppm, corresponding to the five equivalent Cp carbons and two identical carbonyls, respectively. Unlike the rest of the complexes, the $^{13}C$ spectrum of complex **4** shows two Cp peaks at 87.97 and 87.95 ppm and two CO peaks at 195.99 and 195.59 ppm. This is a further indication that the Cp as well as CO ligands are diastereostopic. The $^{13}C$ NMR spectrum of **8** clearly show peaks corresponding to the allylic carbon atoms at ca. 135.17 and 118.57 ppm for the β and γ-carbon atoms, respectively.

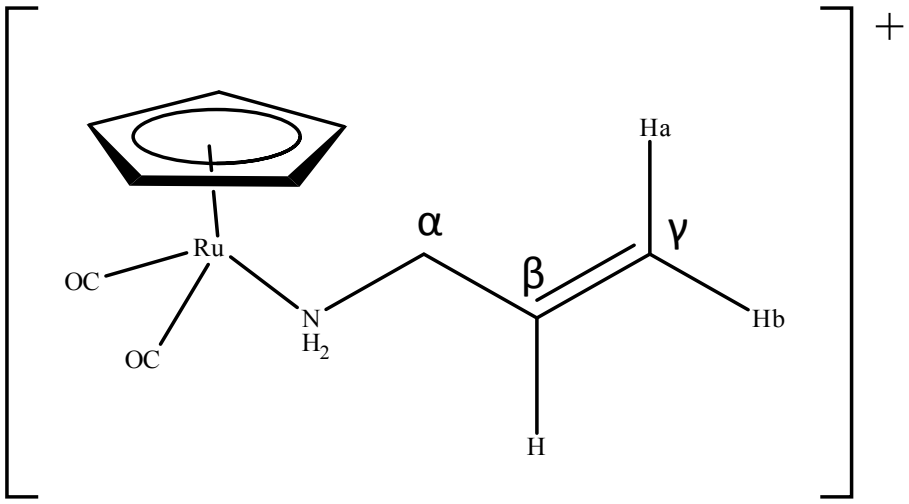



**Figure 2:** structure of 3-aminopropyl-1-ene (allylamine**)** ruthenium complex, **8**

The IR spectra of the complexes **1-9** showed ν(CO) absorption bands in the expected region for terminal carbonyl groups for amine coordinated metal complexes [37,39,40,47]. The ν(CO) absorption bands were observed as two strong peaks, one in the region ca. 2061 - 2049 $cm^{-1}$ for

the asymmetric CO stretching vibrations and one at ca. 2016 - 1987 $cm^{-1}$ for symmetric CO stretching vibrations. It is worth noting that the symmetric CO stretching frequency for the cyclohexylamine complex **1** is lower than those observed for the complexes **2** – **7**, which have the phenyl ring as a substituent of the amine group. This can be attributed to the fact that the cyclohexyl group, a strong electron donor, increases electron density at the ruthenium centre from the amine sigma donation. The electrons are thus passed to the CO π* orbital and reflected in a decreased νCO stretching frequency, which corresponds to weaker CO bonds. The symmetric νCO stretching frequency for complex **6** is greater than for complex **5,** probably because the nitrile group substituent in the para position of the phenyl ring in **6** is electron withdrawing, while the methoxy group, a para-substituent in the phenyl ring in complex **5**, is electron donating.

The IR spectra also show two characteristic absorption bands in the regions ca. 3325 – 3270 $cm^{-1}$ and 3293 – 3264 $cm^{-1}$ which correspond to the $NH_2$ asymmetric and symmetric peaks respectively. These bands are found at lower wavenumbers than for the uncoordinated ligands, due to coordination of the amine functionality to the metal centre and likely due to the participation of the $NH_2$ protons in hydrogen bonding.

### *3.2 Molecular Structure of complexes 3 and 8*

Single crystal X-ray diffraction was used to determine the molecular structures of complexes **3** and **8**. They crystallize as white solids in the monoclinic space group $P2_1/n$. Complex **3** has two cationic molecules, $[CpRu(CO)_2C_6H_5CH_2NH_2]^+$, and two counter-anions, $BF_4^-$, in its asymmetric unit, while complex **8** has one cationic molecule, $[CpRu(CO)_2CH_2CHCH_2NH_2]^+$, and one counter anion in its asymmetric unit. The molecular diagrams of the complexes are provided in Figs. 3 and 4, while Table 4 gives a comparison of important bond distances and angles.

**Table 4:** Selected inter-atomic distances (Å) and angles (°C) for complex **3** and **8**

| **Bond Parameter** | **3 (Molecule 1)** | **3 (Molecule 2)** | **8** |
|---|---|---|---|
| *Cg−Ru | 1.866 | 1.867 | 1.870 |
| Ru−N | 2.146(1) | 2.138(2) | 2.140(1) |
| N−C | 1.488(2) | 1.479(3) | 1.486(2) |

| Bond Parameter | 3 (Molecule 1) | 3 (Molecule 2) | 8 |
|---|---|---|---|
| NC−C | 1.506(3) | 1.505(3) | 1.492(3) |
| C=C | – | – | 1.316(3) |
| Benzene ring C−C | 1.393(3), 1.377(3) | 1.389(3), 1.386(3) | – |
| | 1.392(3), 1.374(4) | 1.387(3), 1.380(3) | – |
| | 1.394(3), 1.373(3) | 1.389(3), 1.382(3) | – |
| *Cg−Ru−N | 122.68 | 122.84 | 124.11 |
| Ru−N−C | 118.9(1) | 119.4(1) | 115.60(2) |
| N−C−C | 112.3(2) | 113.0(2) | 113.1(1) |
| *Cg−Ru−N−C | 150.10 | 162.57 | 71.40 |
| Ru−N−C−C | 173.4(1) | 176.1(1) | 179.3(1) |

*Cg is the centroid for C1-C5 of the Cp ring

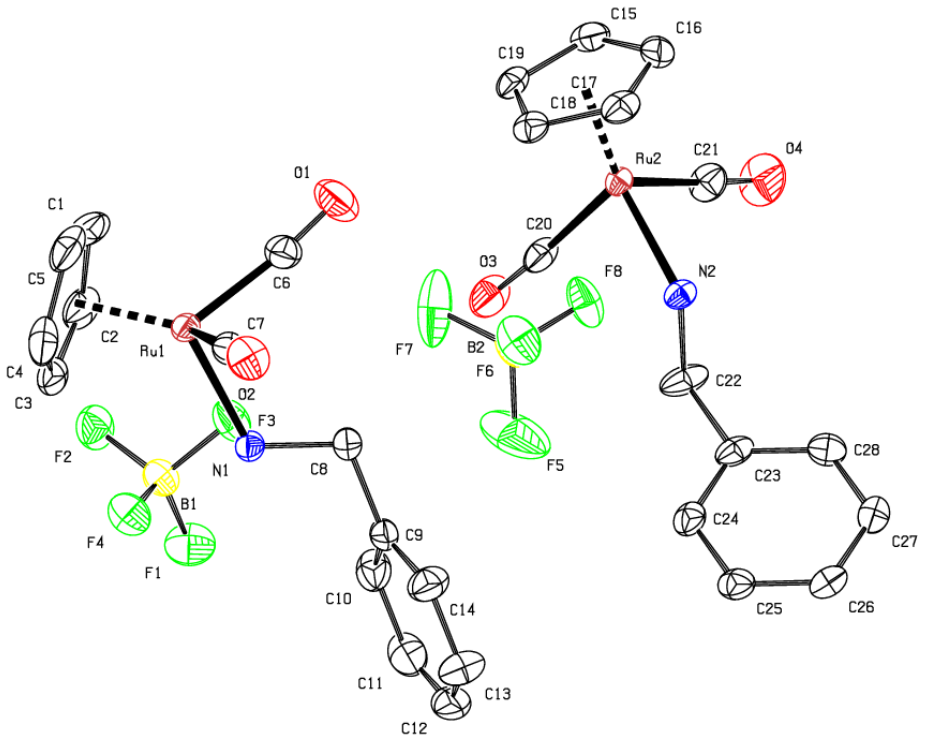



**Figure 3:** The molecular structure of complex **3** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are not shown for clarity

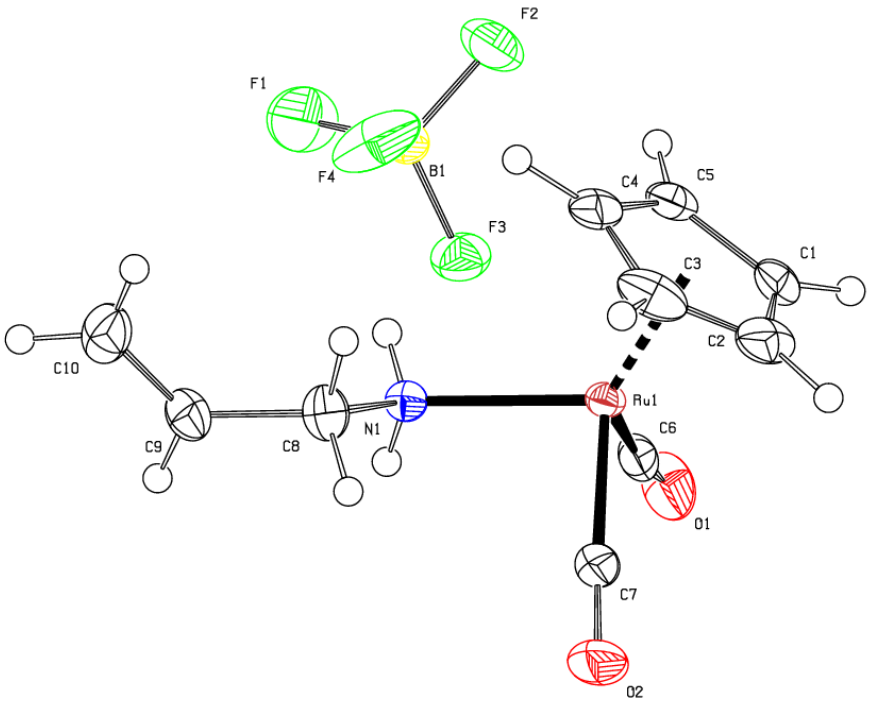



**Figure 4:** The molecular structure of complex **8** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are not shown

In both cases, the amine ligands are linked to the ruthenium centre of the $CpRu(CO)_2$ moieties via the nitrogen atoms by sigma bonds giving distorted octahedral coordination geometries around the ruthenium centres; with the Cp ligand occupying three sites, while the remaining three sites are occupied by the two carbonyl ligands and the amine. Ruthenium is, therefore, coordinated in the known "pseudo-octahedral three-legged piano-stool" fashion with the Cp ligand occupying the apical position of the stool (Figs. 3 and 4). The Ru−N bond lengths for the two complexes are almost equal and are comparable to similar Ru−N bond lengths previously reported for $\eta^5$-cyclopentadienyldicarbonylruthenium(II) n-alkanamine complexes, 2.139(1) Å for $[CpRu(CO)_2NH_2CH_2CH_3]BF_4$, 2.1406(12) Å for $[CpRu(CO)_2NH_2(CH_2)_2CH_3]BF_4$ and 2.139(1) Å for $[CpRu(CO)_2NH_2(CH_2)_3CH_3]BF_4$ [37]. As is expected, due to the larger ionic radius of ruthenium, the Ru−N and Cg−Ru (Cg is the centroid of the Cp rings) bonds lengths in complex **8** are greater than those reported for the analogous iron complex $CpFe(CO)_2NH_2CH_2CHCH_2]BF_4$, Cg−Fe (1.715) Å and Fe−N (2.018) [39]. The coordinated allylamine bond lengths (N−C (1.484(8)), $C-C_{allyl}$ (1.498(8)) and C=C (1.300(9)) Å) in the iron complex are comparable to those found for complex **8**. This implies that the metal center does not affect the bond lengths within the allylamine ligand. As previously observed for $CpFe(CO)_2NH_2CH_2CHCH_2]BF_4$ [39], the C=C bond distance in the

allylamine coordinated to the ruthenium center is slightly shorter than the formal C=C double bond (1.34 Å) [40,48]; but comparable with the calculated distances for a terminal C=C bond; 1.315 Å for ethylene, 1.316 Å for propene and 1.321 Å for 2-methylpropene [49]. It is worth noting that the C−C bond lengths in the phenyl ring for the two independent cationic molecules in the asymmetric unit of complex **3** are comparable to the actual bond lengths in the benzene ring (1.39 Å). The phenyl ring C−C bond lengths in the two molecules of complex **3** are not the same (Table 8). Alternate C=C bond distances in molecule 1 of complex **3** differ from one another by about 0.018 Å, while those in molecule 2 differ by about 0.005 Å**.** The bond angles of complex **3** and **8** are comparable to each other and to those of the earlier reported $\eta^5$-cyclopentadienyldicarbonyliron(II) allylamine complex; Fe−N−C (117.0(3)) Å, Cg−Fe−N (123.4) Å and N−C−$C_{allyl}$ (112.3(4) Å) [39] and $\eta^5$-cyclopentadienyldicarbonylruthenium(II) amine complexes; Cg−Ru−N (122.92 – 124.08 Å), Ru−N−C (113.2 – 118.53 Å) [37]. Figures 5 and 6 show crystal packing diagrams for complexes **3** and **8** respectively.

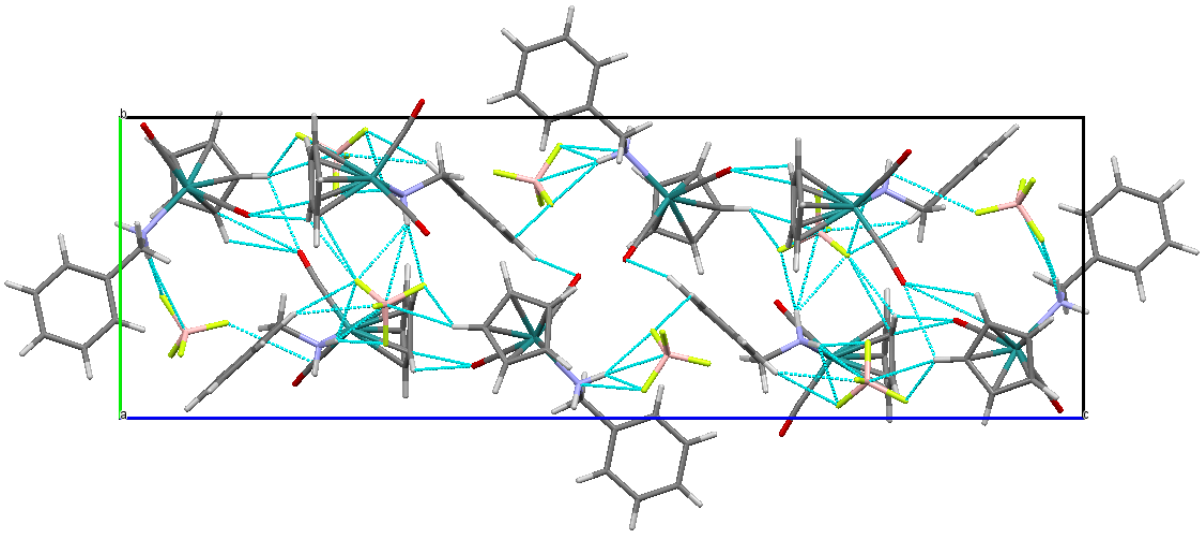


**Figure 5:** Crystal packing of complex **3,** as viewed along b-axis, showing hydrogen bonds and other intermolecular interactions

In the crystal structure of complex **3**, the cations are directly linked together by Cp ring carbon and hydrogen atoms interacting with oxygen atoms of the neighbouring cationic molecule; C···O and H···O (Fig. 5), while the cations and anions are linked by hydrogen bonds (N−H···F), as well as C($C_6H_5$)−H···B, C−H···F, O−C···F, N−H. . .B and C(Cp) −H···B. In complex **8**, the cations mainly interact with one another through the tetrafluoroborate anions via N−H···F, C−O···F, O−C···F, C(Cp)−H···F, C(Cp)−H···B and N−H···B bonds, as illustrated in Fig. 6.

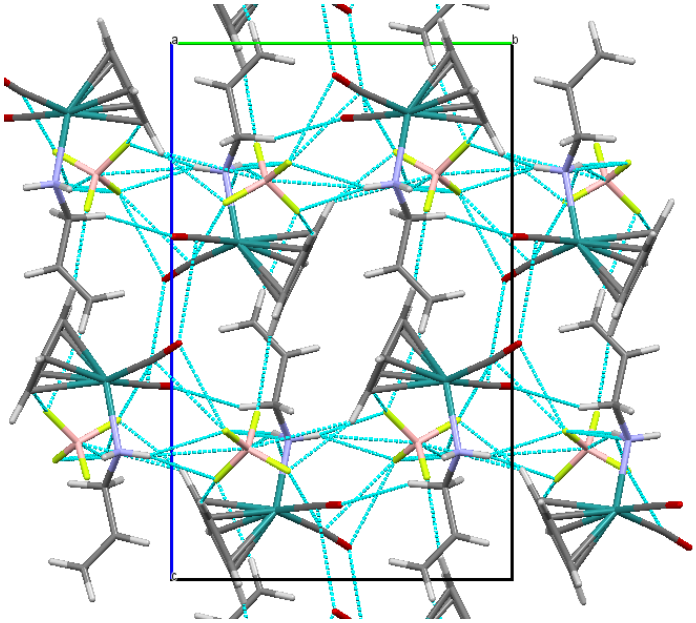


**Figure 6**: Crystal packing of complex **8,** as viewed along a-axis, showing hydrogen bonds and other intermolecular interactions

### *3.3 Catalytic oxidation of styrene*

Oxidative cleavage of the olefinic carbon-carbon bond in styrene has been achieved in excellent conversions and benzaldehyde yields using sodium periodate ($NaIO_4$) as the co-oxidant and $\eta^5$-cyclopentadienyldicarbonylruthenium(II) complexes as catalysts. Acetonitrile/water (1:1 v/v; 6 mL) was selected as the solvent system, because of the need to have all the reagents and catalysts in the same phase. The solubility of the substrate and oxidant and, hence, homogeneity of the system depends on temperatures higher than room temperature.

At room temperature, 22 °C, and a temperature of 40 °C, over 99% conversion and 90% benzaldehyde yield is achieved in 18 and 17 h respectively (Fig. 7). At 60 °C, a temperature at which a homogeneous mixture is obtained, over 99% conversion, 85% benzaldehyde and 2% styrene oxide yields are achieved in 3 h. The temperature of 60 °C was chosen for all catalytic test reactions, since it gave homogenous mixtures and high conversion in a shorter time.

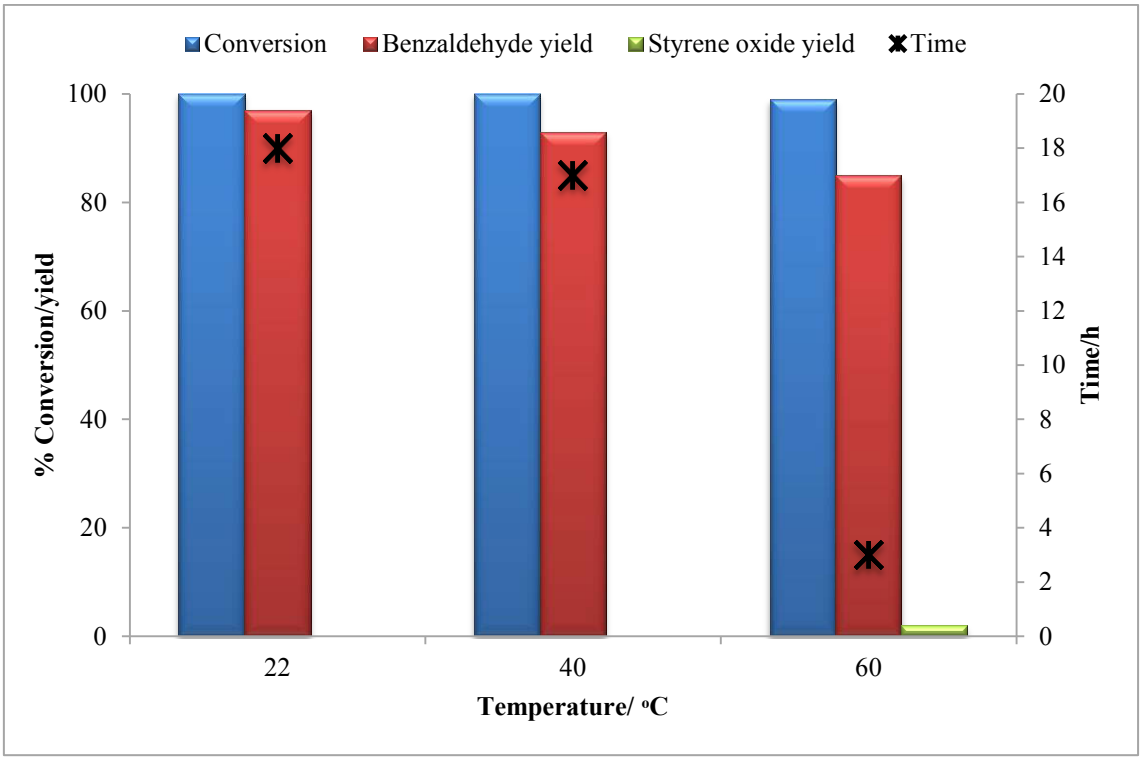
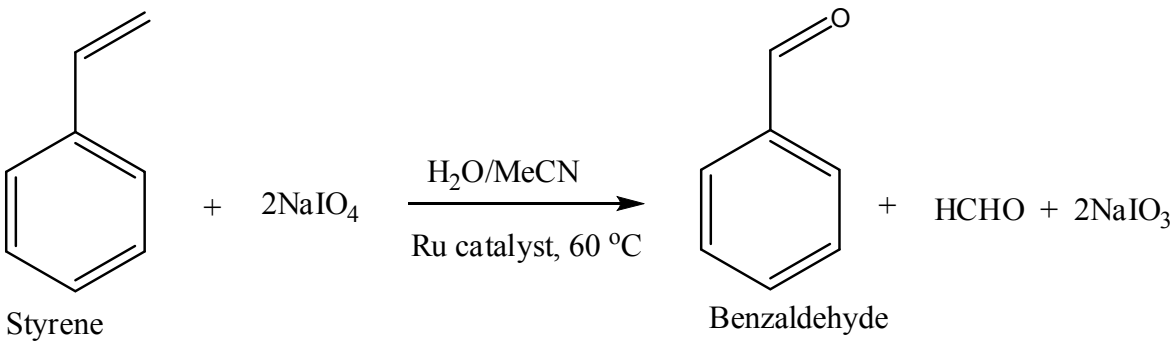



**Figure 7:** Effect of temperature on the conversion and yield for the ruthenium complex-catalyzed oxidation of styrene; Reaction conditions: 0.478 mmols styrene, 3 equiv. $NaIO_4$, 2.5 mol% [RpCHA]B, $CH_3CN$:$H_2O$ (3 mL:3 mL). Time to achieve highest conversion is given in hours

The oxidative cleavage of styrene with 3 equivalents $NaIO_4$ in the absence of the ruthenium complexes affords 32% conversion and 21% benzaldehyde yield in 10 h, while in the presence of 2.5 mol % of the ruthenium complexes, the conversion and benzaldehyde yield rises to 99 % and 85% respectively in 3 h (Fig 8). This is a clear indication that the ruthenium complexes reported herein are effective catalysts for the oxidative cleavage of the olefinic carbon-carbon bond in styrene (Scheme 2).




**Scheme 2:** General equation for the oxidative cleavage of styrene to benzaldehyde

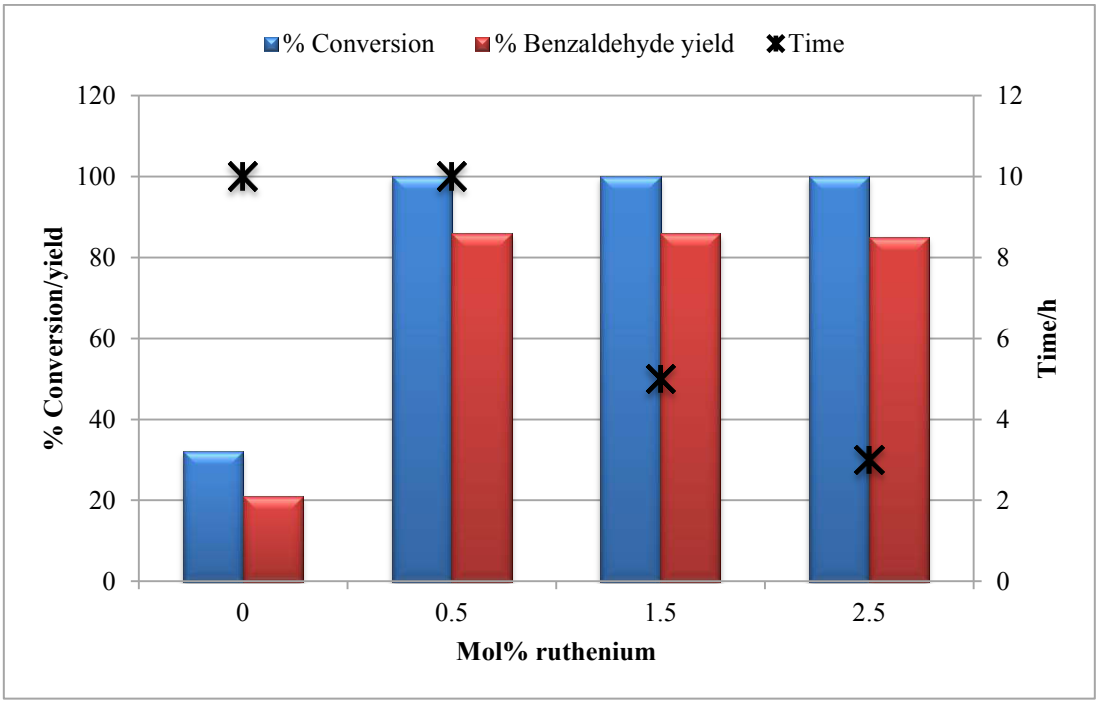



**Figure 8:** Effect of catalyst concentration on the oxidative cleavage of the olefinic double bond in styrene. Reaction conditions: 0.478 mmols styrene, 3 equiv. $NaIO_4$, $CH_3CN$:$H_2O$ (1:1; 6 mL) at 60 °C. Time taken to achieve highest conversion is given in hours

It was noted that the conversion and yield, and the time needed for the reaction to go to completion, is proportional to the amount of the co-oxidant used. Studies done on the effect of co-oxidant concentration on the reaction progress indicate that an excess of the co-oxidant is necessary for the reaction to give 100 % conversion (Fig. 9). This observation augments the step in the proposed mechanism where the intermediate product, the metal diether, requires 'oxygen' to form the benzaldehyde (Scheme 3). Hence, 3 equivalents $NaIO_4$ were selected as the optimum amount of oxidant suitable for the process.

The use of hydrogen peroxide and $K_2S_2O_8$ as co-oxidants in the oxidation of styrene in the presence of the ruthenium complex catalysts was compared with $NaIO_4$. It was observed that $NaIO_4$ gave excellent conversion and yield under the reaction conditions to afford benzaldehyde. Hydrogen peroxide as an oxidant gave good conversion (86 %) but very low yields of benzaldehyde (23 %) and styrene glycol (9 %) in 18 h (Fig. 10). The rest of the product was confirmed to be benzoic acid, an indication that over-oxidation of benzaldehyde had taken place. The styrene glycol is probably formed as an intermediate product which is eventually oxidized to benzaldehyde [50]. The reaction with $K_2S_2O_8$ as an oxidant, for the oxidation of styrene, was noted to have stopped at 2 h giving a maximum of 40 % conversion.

$NaIO_4$ was thus retained as the best primary oxidant for the oxidative cleavage of the olefinic C−C bond.

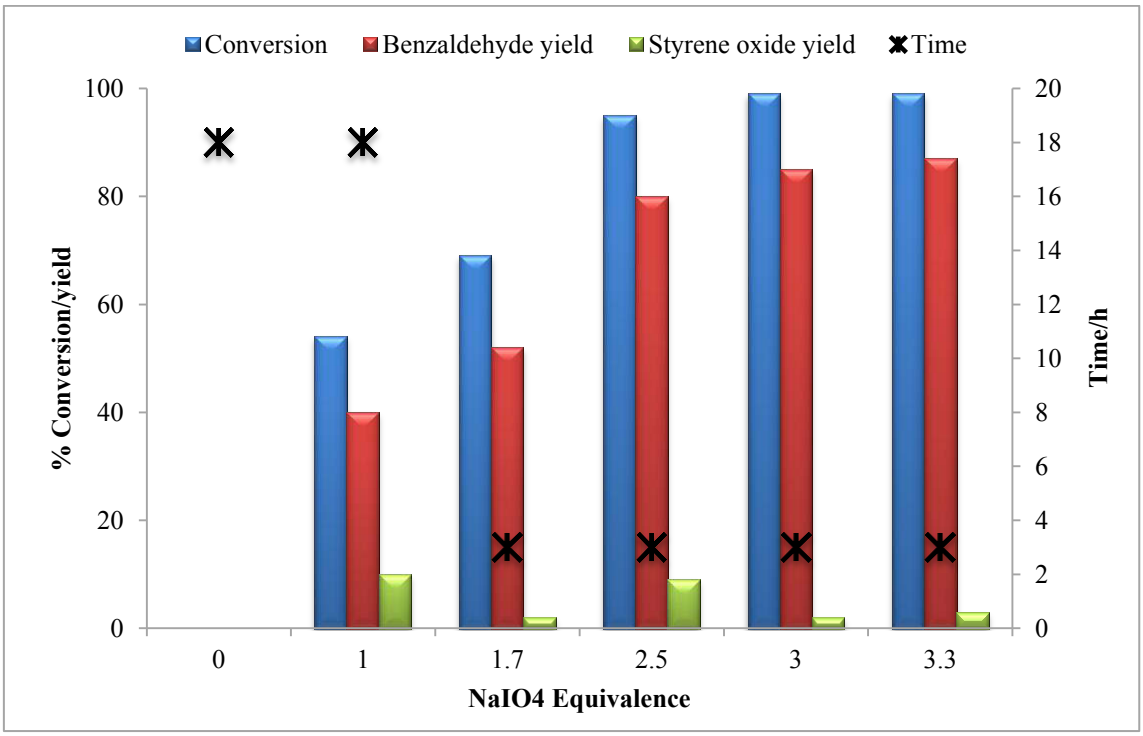
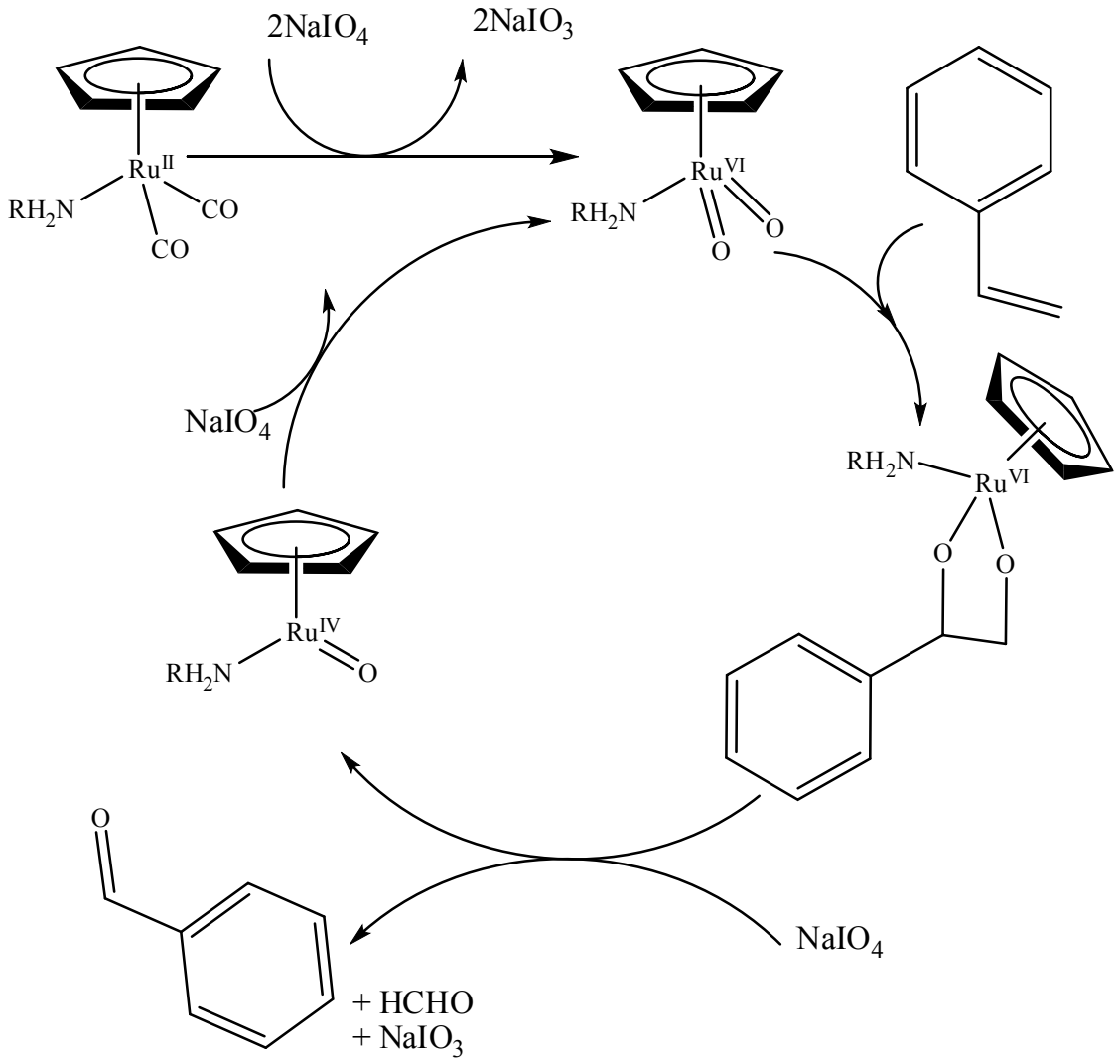



**Figure 9**: Effect of $NaIO_4$ concentration on the % conversion and % benzaldehyde yield for the ruthenium complex-catalyzed oxidation of styrene. Reaction conditions: 0.478 mmols styrene, x equiv. $NaIO_4$, 2.5 mol% [RpCHA]B, $CH_3CN$:$H_2O$ (3 mL:3 mL) at 60 °C. Time taken to achieve highest conversion is given in hours




**Scheme 3:** Proposed mechanism for the ruthenium(II) complex-based catalyzed oxidation of styrene [50]

The effect of basic, acidic and neutral conditions on the catalytic oxidation of styrene was investigated and revealed that the conversion of styrene is highest under neutral and acidic conditions (Fig. 11). This implies that a base is not suitable, while an acid is not essential for the reaction to proceed to completion. Thus, the environmentally more friendly neutral condition was selected for all other tests.

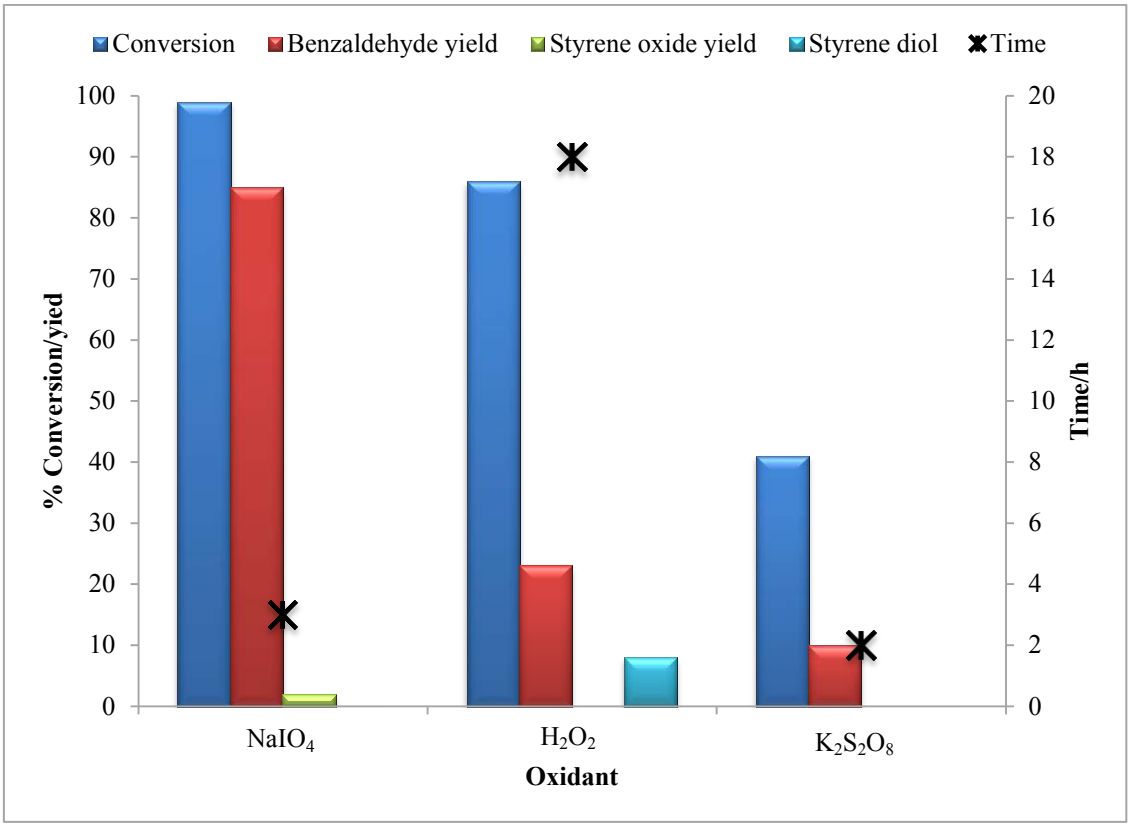



**Figure 10**: Oxidation products from different oxidants for the ruthenium complex-catalyzed oxidation of styrene**.** Reaction conditions: 0.478 mmols styrene, 3 equiv. oxidant, 2.5 mol% [RpCHA]B, $CH_3CN/H_2O$ (3 mL:3 mL) at 60 °C. Time take to achieve highest conversion is given in hours

Investigations on varying the amount of catalyst used for the reaction to go to completion indicated that the time taken decreases with increase in mol% catalyst used (Fig. 8). Once 100 % styrene conversion is achieved, the reaction mixture changes colour from colourless to orange. The catalyst present in the mixture at the end of the reaction was shown to have the ability to catalyze the oxidation of fresh styrene to give 100 % conversion and more than 99 % benzaldehyde yield. Furthermore, complete conversion was achieved within a shorter time with the 're-used' catalyst than when fresh catalyst was used. This may imply that the $\eta^5$-cyclopentadienyldicarbonylruthenium(II) complex is not the catalyst itself, but a catalyst precursor which is not deactivated at the end of the reaction, thus, a more catalytically active intermediate species is formed .

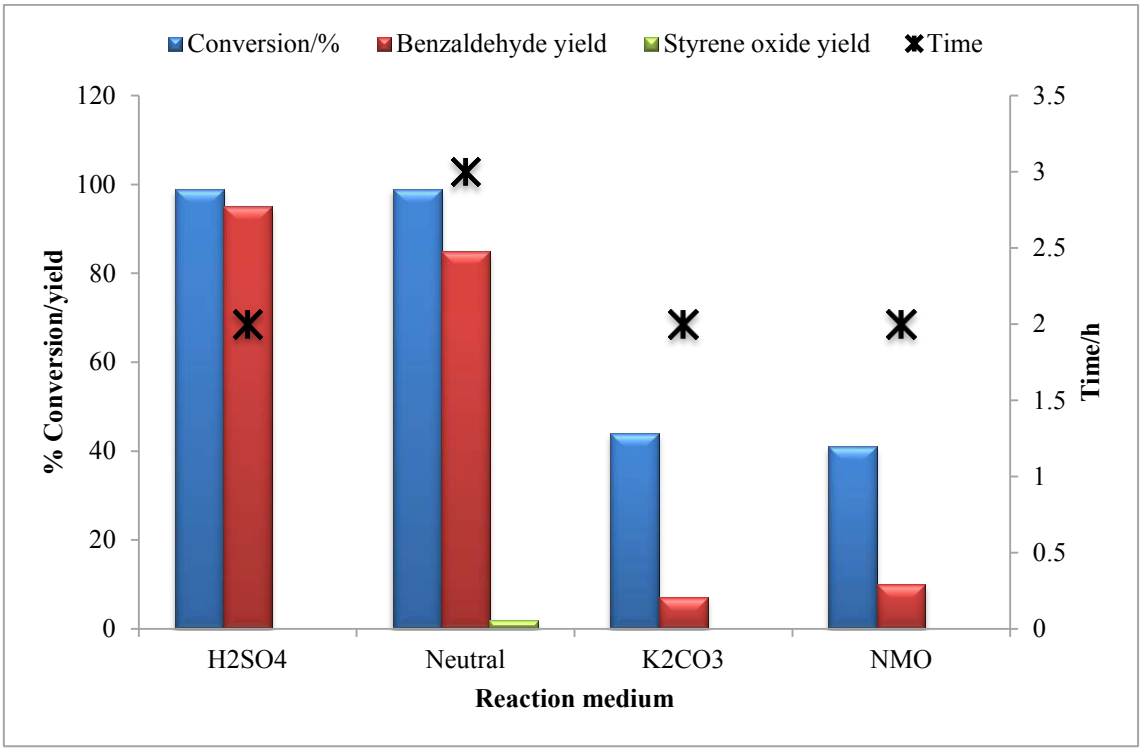



**Figure 11:** Effect of acidic, basic and neutral conditions on the ruthenium complex catalyzed oxidation of styrene. Reaction conditions: 0.478 mmols styrene, 3 equiv. $NaIO_4$, 2.5 mol% [RpCHA]B, $CH_3CN$:$H_2O$ (1:1; 6 mL) at 60 °C. Time taken to achieve highest conversion is given in hours.

The UV-VIS spectrum obtained for the dark orange coloured compound recovered at the end of the reaction showed a peak at ca. 360 nm (Fig. 12). A similar peak was observed by Goldstein and Drago, at 365 nm, and was assigned to the $Ru^{VI}=O$ species [51]. Their study was based on the hydroxylation of methane by hydrogen peroxide as the co-oxidant and cis-$[Ru(dmp)_2S_2](PF_6)$ (dmp = 2,9 dimethyl-I, l0-phenanthroline, S = $Me_3CN$ or $H_2O$) as the catalyst. The difference in peak positions may be attributed to the different coordination environments of the complexes reported herein and those used by Goldstein and Drago. This peak may, therefore, be assigned to a dioxo-ruthenium(VI) complex species formed as an intermediate in the catalytic oxidation of styrene. Noteworthy, the peak at 360 nm in the UV-VIS spectrum was absent in the spectra of the fresh catalyst and the reaction mixtures sampled at 30 min intervals (Fig 12). This implies that the dioxo-ruthenium species is highly active and hence only seen in solution once styrene is depleted (Scheme 3). It is worth noting that the peaks observed by Goldstein and Drago at 395 and 425 nm assignable to $Ru^{III}$ and $Ru^{IV}=O$ respectively, were absent in the UV-VIS spectra of the recovered catalyst and the reaction mixtures examined (Fig. 12). This could imply that if the catalytic oxidation of styrene involves

the formation of $Ru^{III}$ and the postulated $Ru^{IV}$=O species, these are very rapidly oxidized to $Ru^{VI}$=O, and hence not detected.

The solid state IR spectrum obtained for the recovered catalyst showed new peaks at 793, 769 and 728 $cm^{-1}$ possibly assignable to the symmetric and asymmetric stretches of Ru=O bonds of Ru(VI) dioxo species [52]. No peaks were observed in the carbonyl region (between 2056 and 1998 $cm^{-1}$), an indication that the recovered catalyst does not contain coordinated CO ligand. A $^1$H NMR spectrum obtained for the recovered catalyst showed a signal at ca. δ 5.67 ppm assignable to the 5 Cp protons and a peak at ca. δ 4.00 ppm assignable to the amine nitrogen protons. Since the proposed Ru(VI) dioxo species ($d^2$) would be paramagnetic in nature, the observed Cp and amine nitrogen proton signals in the $^1$H NMR spectrum suggests that there is a diamagnetic species.

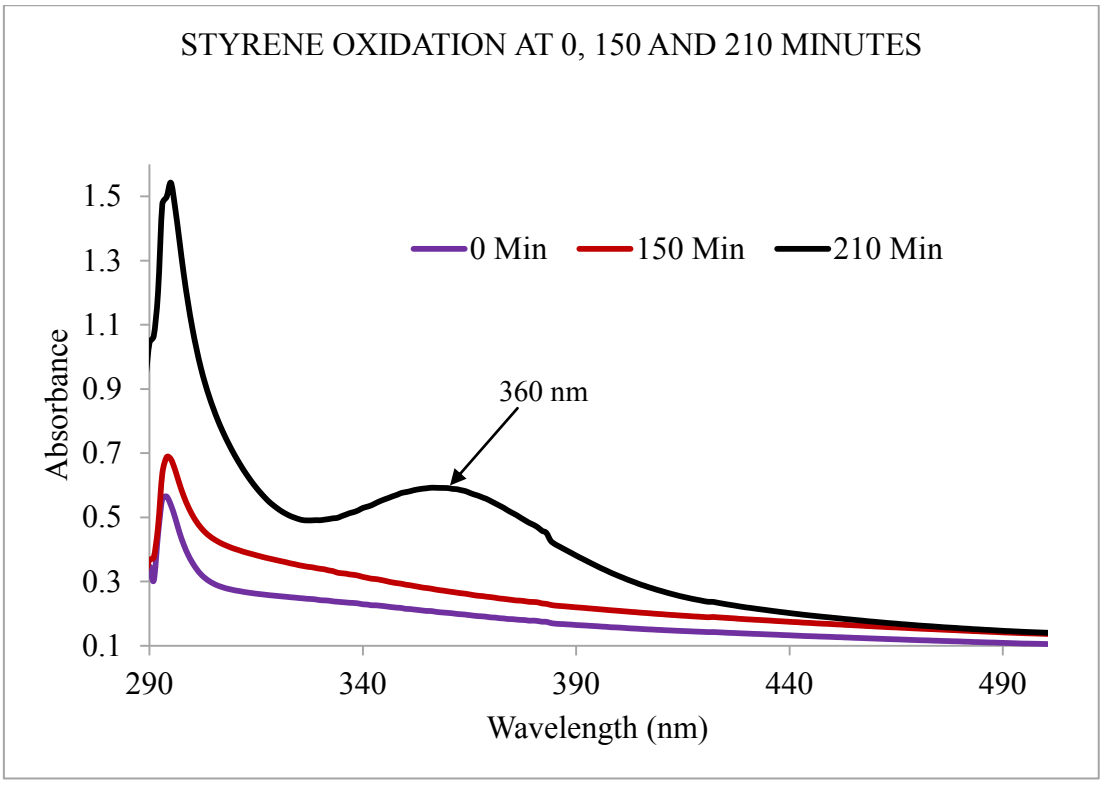



**Figure 12:** Electronic spectra of samples obtained at different times into the catalyzed reaction

Table 5 show the results for the catalytic oxidation by 0.5 mol% catalyst of the various ruthenium complexes under the optimized conditions.

**Table 5**: Ruthenium complexes (0.5 mol%) catalyzed oxidative cleavage of the styrene olefinic bond[a]

| Complex | Time (h)[b] | % Yield | % Conversion | TON | TOF/h |
|---|---|---|---|---|---|
| [RpCHA]B (**1**) | 10 | 86 | 100 | 172 | 17 |
| [RpBA]B (**3**) | 14 | 81 | 91 | 162 | 11 |
| [RpMBA]B (**4**) | 12 | 87 | 100 | 174 | 14 |
| [RpMeOBA]B (**5**) | 3 | 99 | 99 | 198 | 66 |
| [RpAMBN]B (**6**) | 3 | 100 | 94 | 200 | 65 |
| [RpiPA]B (**9**) | 16 | 94 | 100 | 188 | 12 |
| [RpMeNH2]B (**10**) | 9 | 87 | 98 | 174 | 19 |
| [RpHMDA]B (**11**) | 2 | 99 | 99 | 198 | 100 |
| No catalyst | 10 | 21 | 32 | 0 | 0 |

[a]Reaction conditions: 0.478 mmols styrene, 3 equiv. $NaIO_4$, $CH_3CN/H_2O$ (1:1; 6mL) at 60 °C.

[b]Time taken to achieve highest conversion is given in h.

All the complexes tested afforded more than 90 % styrene conversion and over 80 % benzaldehyde yield. It is noteworthy that the oxidation process in the presence of the ruthenium dinuclear complex, $[RpHMDARp]^{2+}$ (**11**), has the highest turnover frequency (TOF) of 100 $h^{-1}$. This implies that the ruthenium centre is directly involved in the oxidation process, since the mol% in terms of ruthenium is twice as high as that for the mononuclear complexes; probably the oxo-species are formed at both metal centres thus doubling the catalysis rate. It is interesting to note that despite the complexes containing 4-methoxybenzyl amine (**5**) and 4-aminomethylbenzonitrile (**6**) being mononuclear, with the ligand in **5** being more basic than that in **6**, they demonstrated excellent activities with almost equal TOFs of 66 $h^{-1}$ and 65 $h^{-1}$ respectively. In contrast, the TOF for the benzylamine complex (**3**) was noted to be 11 $h^{-1}$; the phenyl ring increases the basicity of the amine thus increasing the π-back-bonding effect on the CO ligand and eventually strengthening the M–CO bond. This would decrease the rate at which the CO ligand is lost in the $Ru^{II}$ to $Ru^{VI}$ oxidation step, hence decreasing the reaction rate. This observation implies that the loss of CO, which is dependent on the electronic effect of the ligand, and the oxidation of $Ru^{II}$ to $Ru^{VI}$ steps may be rate determining in forming the working catalyst in the oxidative cleavage of the styrene olefinic double bond. It is worth noting that low TOFs, 12 $h^{-1}$ and 14 $h^{-1}$, were observed for the complexes containing isopropyl amine (**9**) and α-methylbenzyl amine (**4**), respectively, compared to 19 $h^{-1}$ observed for the methylamine containing complex (**10**). This may be due to, in addition to the mentioned factors, steric hindrance on the metal centre caused by the isopropyl amine and α-methylbenzyl amine, thus blocking the accessibility of the metal centre by the co-oxidant and the substrate.

The oxidation process catalyzed by 2.5 mol % of catalyst **1,** with the cyclohexylamine ligand, formed styrene oxide in addition to benzaldehyde. The complexes **3**, **4**, **5** and **6**, which contain a phenyl ring in the amine ligand, form benzaldehyde in high yield but styrene oxide is not observed. The expected biproduct,HCHO, was found in all reactions.

## *4. Conclusion*

The $\eta^5$-cyclopentadienyldicarbonylruthenium(II) amine complexes, $[CpRu(CO)_2NH_2R]BF_4$, have been successfully synthesized. The amine ligands are linked to the ruthenium centre by a σ-bond through the nitrogen atom. The 4-methoxybenzyl amine, 4-aminomethylbenzonitrile and allylamine preferentially bind to the metal centre via the amine nitrogen. Some of the complexes have exhibited excellent catalytic activity in the oxidation of styrene with $NaIO_4$ to give up to 99 % benzaldehyde yield. The "pseudo-octahedral three-legged piano-stool" structure exhibited by the complexes seems to favour the formation of the cis-dioxo ruthenium species required for the formation of the important intermediate 2 + 3 metal diether ring [23]. The configuration displayed by the ruthenium complexes favour the oxidative cleavage of the olefinic C−C bond of styrene and thus the formation of benzaldehyde in high yield. Bulky amine ligands seem to reduce the catalytic activity of the complexes. The recovered catalyst is very active in the oxidative cleavage of the olefin double bond of styrene.

**Acknowledgement**

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# CHAPTER 7

## Conclusions

This thesis has described the synthesis, characterization and structural elucidation of new $\eta^5$-cyclopentadienyldicarbonylruthenium(II) and $\eta^5$-pentamethylcyclopentadienyldicarbonylruthenium(II) amine complexes. The possible application of $\eta^5$-cyclopentadienyldicarbonylruthenium(II) amine as catalysts in the oxidation of styrene using sodium periodate as the oxidant, and possible antimicrobial activity against Gram positive and Gram negative bacteria has been explored.

The reaction of $\eta^5$-$C_5H_5Ru(CO)_2I$ and $AgBF_4$ gives different products depending on; the solvent used, temperature of the reaction and the quantity of $AgBF_4$ used. Two polymorphs of the iodo-bridged ruthenium complex $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2I\}BF_4$ have been successfully isolated from two different reactions, characterized and their crystal structures and packing fully elucidated for the first time. The reaction of $\eta^5$-$C_5H_5Ru(CO)_2I$ with a slight excess $AgBF_4$ in THF at 0 °C affords the iodo-bridged ruthenium complex $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2I\}BF_4$, **I**. A different polymorph, **II**, of the iodo-bridged ruthenium complex is formed when $\eta^5$-$C_5H_5Ru(CO)_2I$ and $AgBF_4$, mole ratio of 1:1, reacts in methylene chloride at room temperature and atmospheric pressure. The two polymorphs have similar spectral properties, but slightly different melting points due to different crystal packing. The electrospray mass spectrum of the iodo-bridged ruthenium complex shows a fragmentation pattern where the carbonyl ligands are successively lost, leaving the iodo-bridged cationic fragment $\{[(\eta^5\text{-}C_5H_5)_2Ru_2CO]I\}^+$. The molecular structures of the two polymorphs of the iodo-bridged complex were determined by single crystal X-ray crystallography. They have different cell parameters and molecular geometries, crystallizes in a monoclinic crystal system, but with different space groups; P2/c and $P2_1/c$. The molecular structures show that their Ru−I−Ru bond angles are different by 4.93°, while the $CpRu(CO)_2$ moiety is staggered in both polymorphs with the dihedral angles, Cg−Ru···Ru−Cg, differing by 101.98°. The crystals of both polymorphs are stabilized by C−H···F intermolecular interactions. However, their packing patterns are vastly different.

Alternatively, the reaction of $\eta^5$-$C_5H_5Ru(CO)_2I$ with a slight excess (approx. 30% excess) $AgBF_4$ in methylene chloride at room temperature gives the Lewis acid $[\eta^5\text{-}C_5H_5Ru(CO)_2]BF_4$, which subsequently reacts with primary amines and other ligands to give the corresponding ruthenium amine complexes. Thus, new water-soluble 1-alkanaminedicarbonyl($\eta^5$-

cyclopentadienyl)ruthenium(II) tetrafluoroborate complex salts, $[CpRu(CO)_2NH_2R]^+BF_4^-$, (Cp = $\eta^5$-$C_5H_5$ (R = $C_nH_{2n+1}$; n = 0 – 5), have been synthesized by the reaction of the organometallic Lewis acid, $[CpRu(CO)_2]^+BF_4$, with slight excesses of 1-alkanamines, $RNH_2$. The 1-alkanamine complexes are white, air-stable solids whose melting points increase with increase in carbon chain length. The sharp melting points and elemental analysis results revealed that the complexes are pure. NMR and IR spectral analyses showed that the 1-alkanamine ligands are coordinated to the ruthenium metal centre via the nitrogen atom and that an increase in the coordinated ligand carbon chain length weakens the C=O bond of the coordinated carbonyl. Electrospray mass spectral analysis showed that the bond formed between the nitrogen and the metal is strong, since the fragment $[CpRuNH_2R]^+$ was observed to be most abundant, thus most stable. Single crystal X-ray diffraction revealed that the cationic species, $[CpRu(CO)_2NH_2R]^+$, feature a "pseudo-octahedral three-legged piano stool" structure in which the ruthenium centre is coordinated through a sigma bond to the amine N atom and the two carbonyl ligands as the base of the stool and the cyclopentadienyl ring as the apex of the stool. The Ru−N bond lengths slightly increase with increase in the ligand carbon chain length, but are longer compared to the Fe−N bond lengths for the analogous iron complexes. The crystal structure of the complexes are generally stabilized by fairly strong N–H···F and C–H···F intermolecular interactions in addition to other intermolecular interactions.

Five new 1-alkylamine($\eta^5$-pentamethylcyclopentadienyl)dicarbonylruthenium(II) complex salts, $[Cp^*Ru(CO)_2NH_2(CH_2)_nCH_3]BF_4$ ($Cp^* = \eta^5$-$C_5(CH_3)_5$; n = 0 – 4) have been synthesized by the reaction of the Lewis acid, $[Cp^*Ru(CO)_2]BF_4$, with the 1-alkylamines. The complexes are white solids, which readily dissolve in the water and are stable in aqueous state. The Cp* ruthenium complexes melt at a higher temperature than their analogous Cp ruthenium complexes. The spectral analyses showed that the 1-alkanamine ligands are coordinated to the metal centre via the amine nitrogen. High resolution mass spectra of the Cp* complexes salts have proved that they were formed. Furthermore, the molecular structure of the complex $[Cp^*Ru(CO)_2NH_2CH_2CH_3]BF_4$ was determined by single crystal X-ray crystallography, providing proof for the coordination of the ligand as predicted from the spectral analyses. The compound crystallized as white needle-like crystals in a triclinic crystal system, space group P-1, with two molecules the cation $[Cp^*Ru(CO)_2NH_2CH_2CH_3]^+$ and two counter anions $BF_4^-$ in the unit cell. The complex cation also exhibits the pseudo-octahedral "three-legged piano stool" geometry. The crystal structure of the complex is also stabilized by fairly strong N−H···F and C−H···F hydrogen bonds.

The α,α′-diaminoalkane-bridged diruthenium complex salts $\{[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2NH_2(CH_2)_nNH_2\}(BF_4)_2$ (n = 2, 3, 4 and 6; Y = $BF_4$ or $SO_3CF_3$) have been synthesized by the reaction of $[RpNCCH_3]Y$ and $NH_2(CH_2)_nNH_2$ in a 2:1 ratio. The complexes are new and have been fully characterized by IR and NMR spectroscopy, elemental analysis and melting point. The $CpRu(CO)_2$ units are centro-symmetrically bonded to the α,α′-diaminoalkane ligand. The α,α′-diaminoalkane ligands are coordinated to the Ru(II) centres via the amine nitrogen. The molecular structure of the complex $\{[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$ have been determined by single crystal X-ray crystallography and it confirms that the α,α′-diaminoalkane is linking two ruthenium centres of the $\{[(\eta^5\text{-}C_5H_5)Ru(CO)_2$ moiety. Antibacterial activity of the ruthenium(II) amine complexes showed that some of the complexes have excellent antibacterial activity. The ruthenium(II) amine complexes have hgher antibacterial activity than the free, uncoordinated ligand.The coordinated ruthenium metal centre probably triggers antibacterial activity of the non-active ligands, while enhancing the activity of those that are already active. In some cases, the ruthenium complexes showed higher antimicrobial activity against both Gram-positive and Gram-negative bacteria than the known antibiotic, ampicillin (AMP10). Some of the complexes demonstrated broad spectrum antibacterial activity

The water-soluble ruthenium(II) mononuclear complexes $[CpRu(CO)_2NH_2R]BF_4$ [Cp = $\eta^5\text{-}C_5H_5$; R = $-C_6H_{11}$, $-C_6H_5$, $-CH_2C_6H_5$, $-CH(CH_3)C_6H_5$, $-CH_2C_6H_4OCH_3$, $-CH_2C_6H_4CN$, $-C_6H_2(CH_3)_3$, $-CH_2CHCH_2$ and $-CH(CH_3)_2$] have been successfully synthesized and fully characterized by IR, high resolution mass spectroscopy, $^1H$ and $^{13}C$ NMR spectroscopy, and elemental analysis. Despite the fact that some of the ligands, $NH_2CH_2C_6H_4OCH_3$, $NH_2CH_2C_6H_4CN$ and $NH_2CH_2CHCH_2$, are heterofunctional, analysis shows that the ligands bonded to the ruthenium centre of the $CpRu(CO)_2$ moiety through the amine functionality, giving mononuclear complexes. The molecular structures of the complexes $[CpRu(CO)_2NH_2CH_2CHCH_2]BF_4$ and $[CpRu(CO)_2CH_2C_6H_5]BF_4$ were determined by X-ray crystallography and confirm coordination of the ligands through the nitrogen atom of the amine group. The complexes are stable in air and in the aqueous state. Some of the complexes were tested in the catalytic oxidation of styrene, where they demonstrated excellent activity in oxidative cleavage of the olefin C−C bond affording more than 90% styrene conversion and over 85% benzaldehyde yield under the reaction conditions. It is believed that the “pseudo-octahedral three-legged piano-stool” structure exhibited by the complexes favours the cleavage of the styrene olefin C=C bond and thus the formation of benzaldehyde in high yield, via the

formation of the cis-dioxo ruthenium species required for the formation of the intermediate 2 + 3 metal diether ring. The previously synthesized mononuclear 1-methylamine ruthenium complex, $[CpRu(CO)_2NH_2CH_3]BF_4$, is also an excellent catalyst in the oxidative cleavage of the styrene olefinic bond, affording 98% conversion and 87% benzaldehyde yield; implying that the rest of the ruthenium(II) 1-alkylamine complexes synthesized in this study are also potentially good catalysts for the oxidative cleavage of styrene.

Finally, a procedure was determined and a total of 23 new $\eta^5$-cyclopentadienyldicarbonylruthenium(II) complexes synthesized and fully characterized. In all the complexes, the ligands are coordinated to the ruthenium metal centre via the nitrogen atom of the amine group. The ionic nature and presence of the amine group in the complexes renders them soluble and stable in water. The molecular structures of 11 of the synthesized complexes were determined and they reveal that the cationic species, $[CpRu(CO)_2NH_2R]^+$, feature a "pseudo-octahedral three-legged piano stool" geometry, similar to those portrayed by the analogous iron complexes, $[CpFe(CO)_2NH_2R]^+$. The bonding and structures of the complexes have been clearly determined, compared to those of the iron analogues and possible explanations for similarities and differences given.

The antimicrobial activities of some of the $\eta^5$-cyclopentadienyldicarbonylruthenium(II) amine complexes have been determined. Some of the ruthenium complexes have shown better antimicrobial activities against both Gram-negative and Gram-positive bacteria than the uncoordinated ligands. It would be interesting to carry out further studies on the antibacterial antitumor activity of the ruthenium complexes. Coordination of actual antimicrobial drugs to the ruthenium centre of the $CpRu(CO)_2$ moiety and studying their antimicrobial activity would be interesting.

The catalytic activities of the $\eta^5$-cyclopentadienyldicarbonylruthenium(II) amine complexes, in the oxidation of styrene, have been determined. The ruthenium complexes have demonstrated excellent catalytic activity in the oxidative cleavage of the styrene olefinic bond. A possible mechanism for the oxidative cleavage of the olefinic bond in the presence of the ruthenium complex catalysts has been proposed. It would be interesting to study the catalytic activity of these complexes in biphasic solvents and in ionic liquids.

# APPENDICES

**APPENDIX A:** Infrared, Nuclear Magnetic Resonance and Mass Spectroscopy data (in CD)

**APPENDIX B:** Crystal structure tables pertaining to chapters 2 – 6 (in CD)

**APPENDIX C:** Gas chromatography-based calculation of % conversion and % yield (in CD)

**APPENDIX D:** Antimicrobial susceptibility test results – sample photos (in CD)

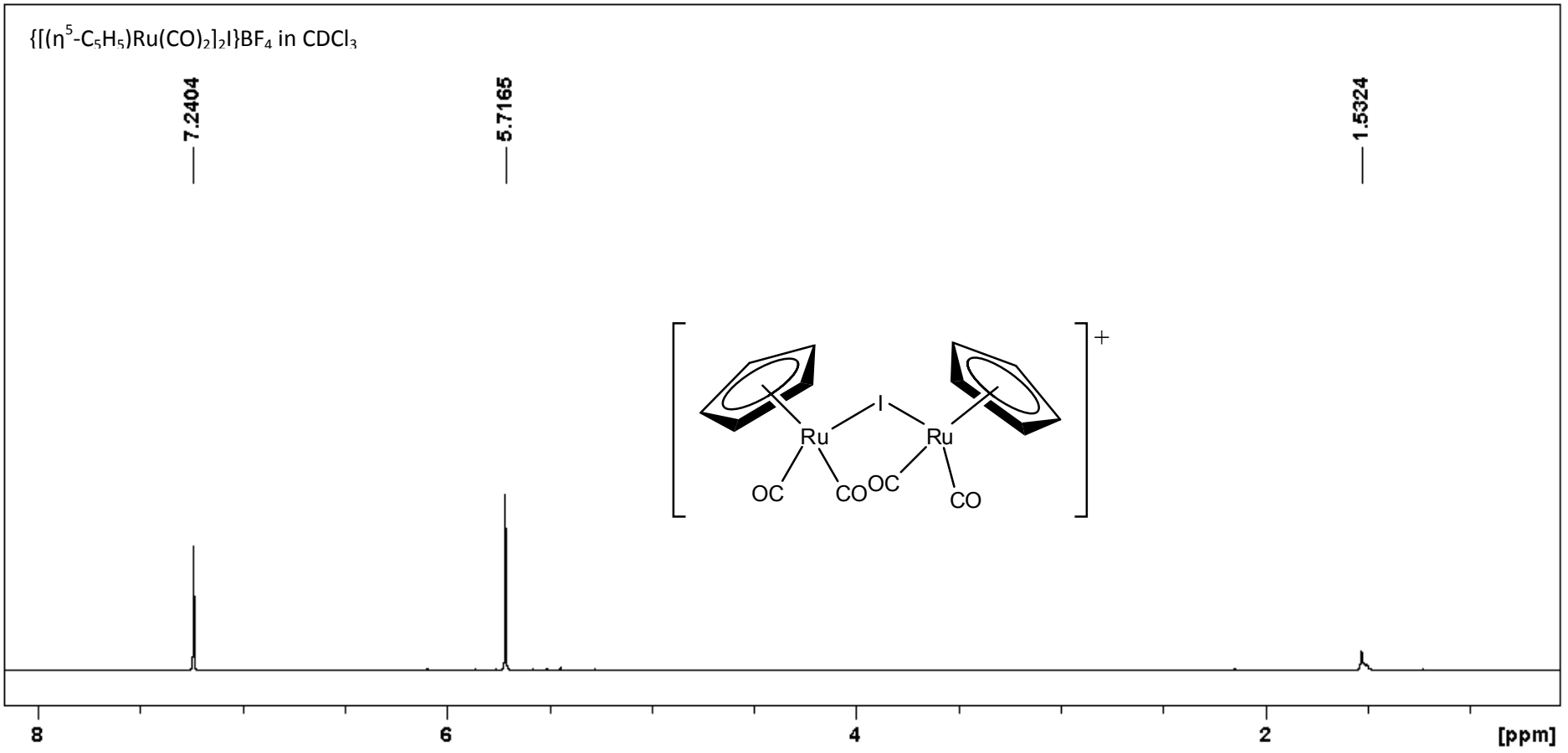
# APPENDIX A

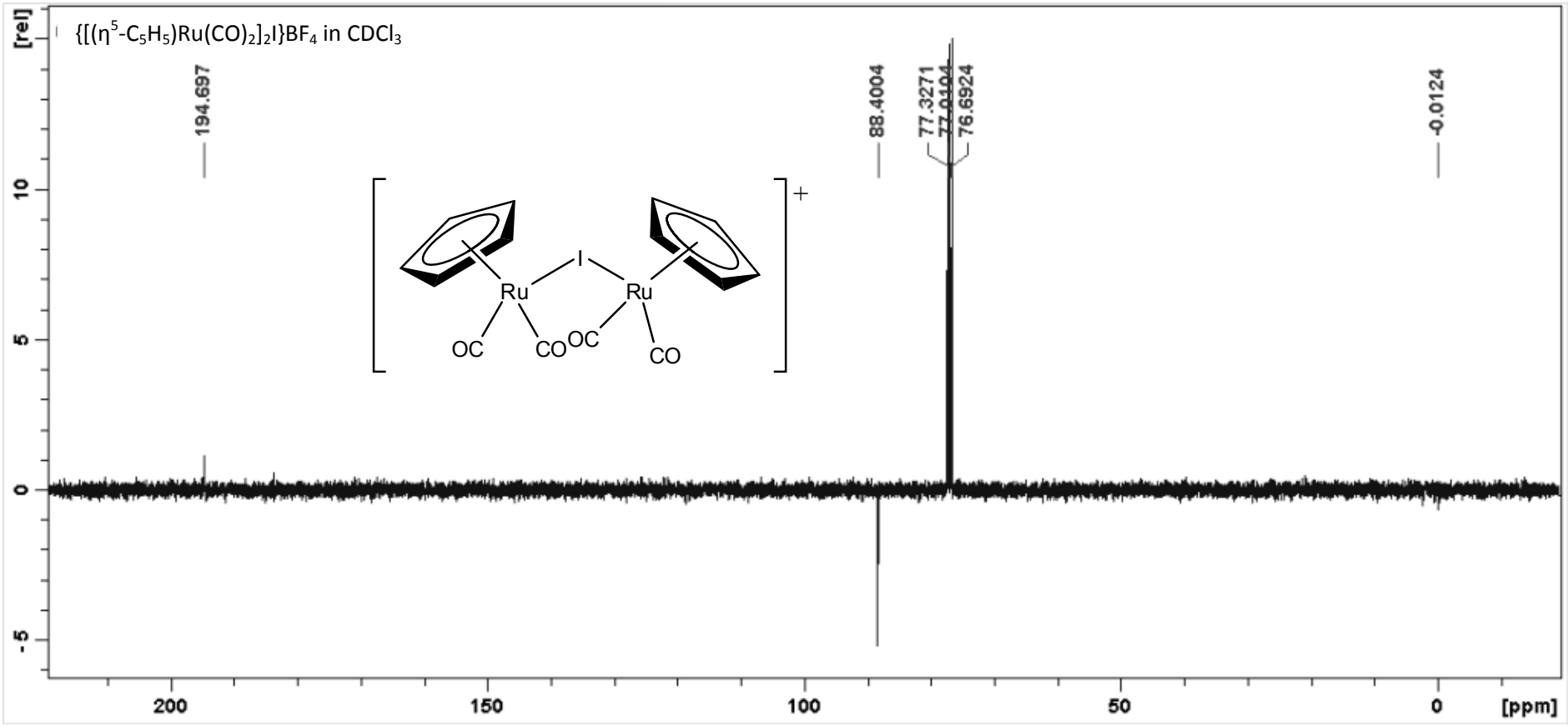
## INFRARED, NUCLEAR MAGNETIC RESONANCE AND MASS SPECTROSCOPY DATA

# Table of Contents

# APPENDIX A

## SPECTRAL DATA PERTAINING TO CHAPTER 2




{[(η5-C5H5)Ru(CO)2]2I}BF4 in CDCl3
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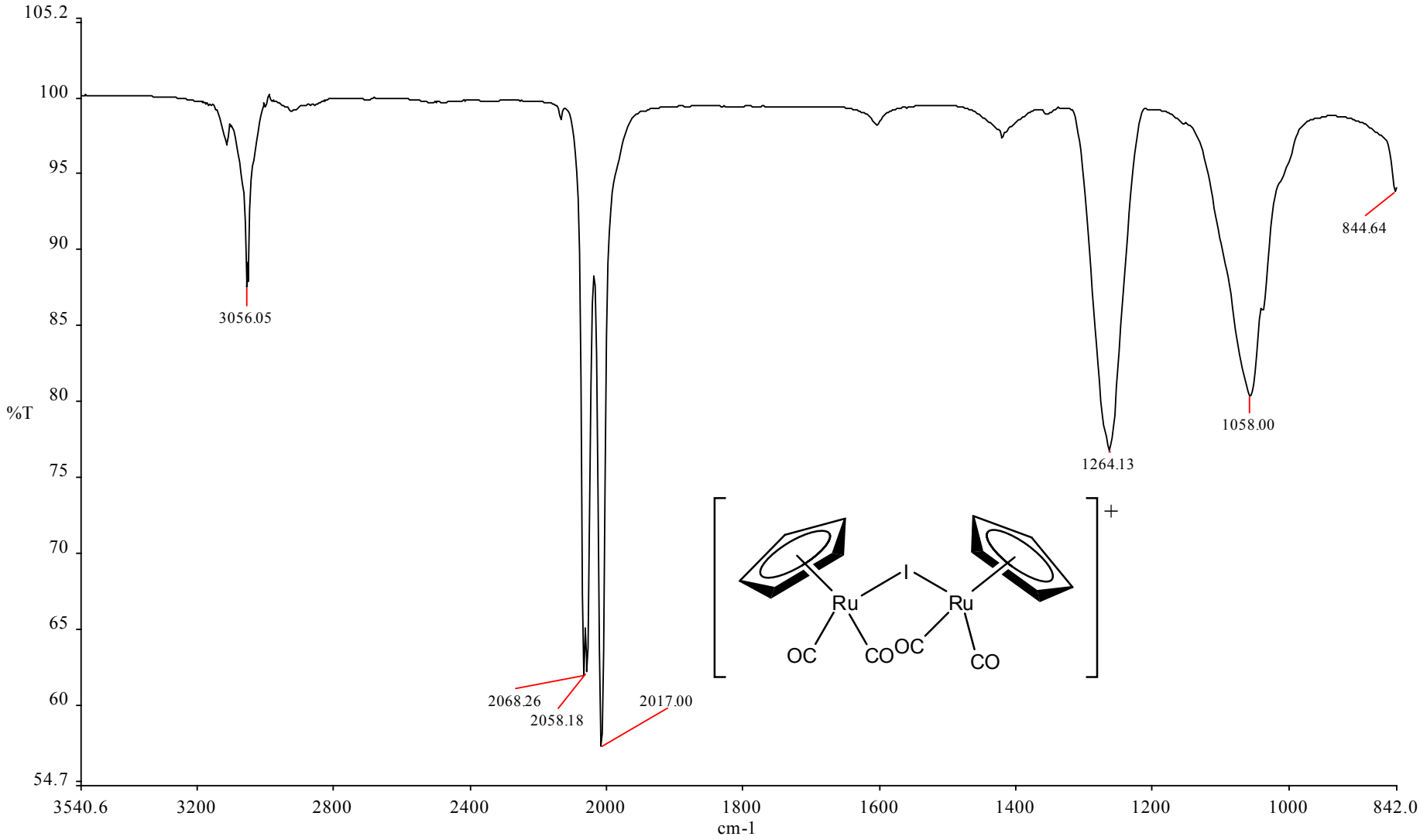
77.0104
76.6924
-0.0124
Ru
I
Ru
OC
CO
OC
CO
+
[rel]
10
5
0
-5
200
150
100
50
0
[ppm]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1264.13
1058.00
844.64
3540.6
3200
2800
2400
2000
1800
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OC
CO
+

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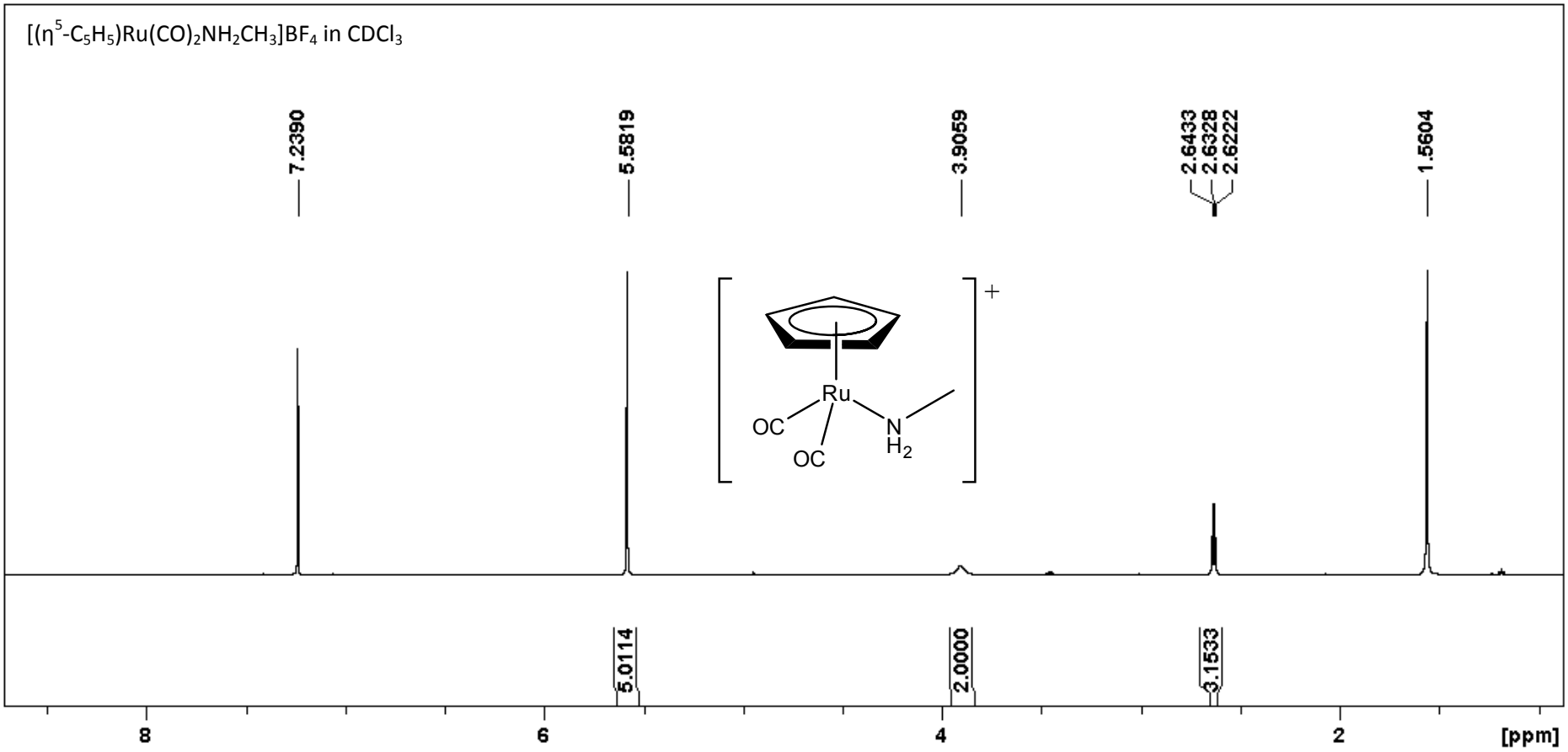

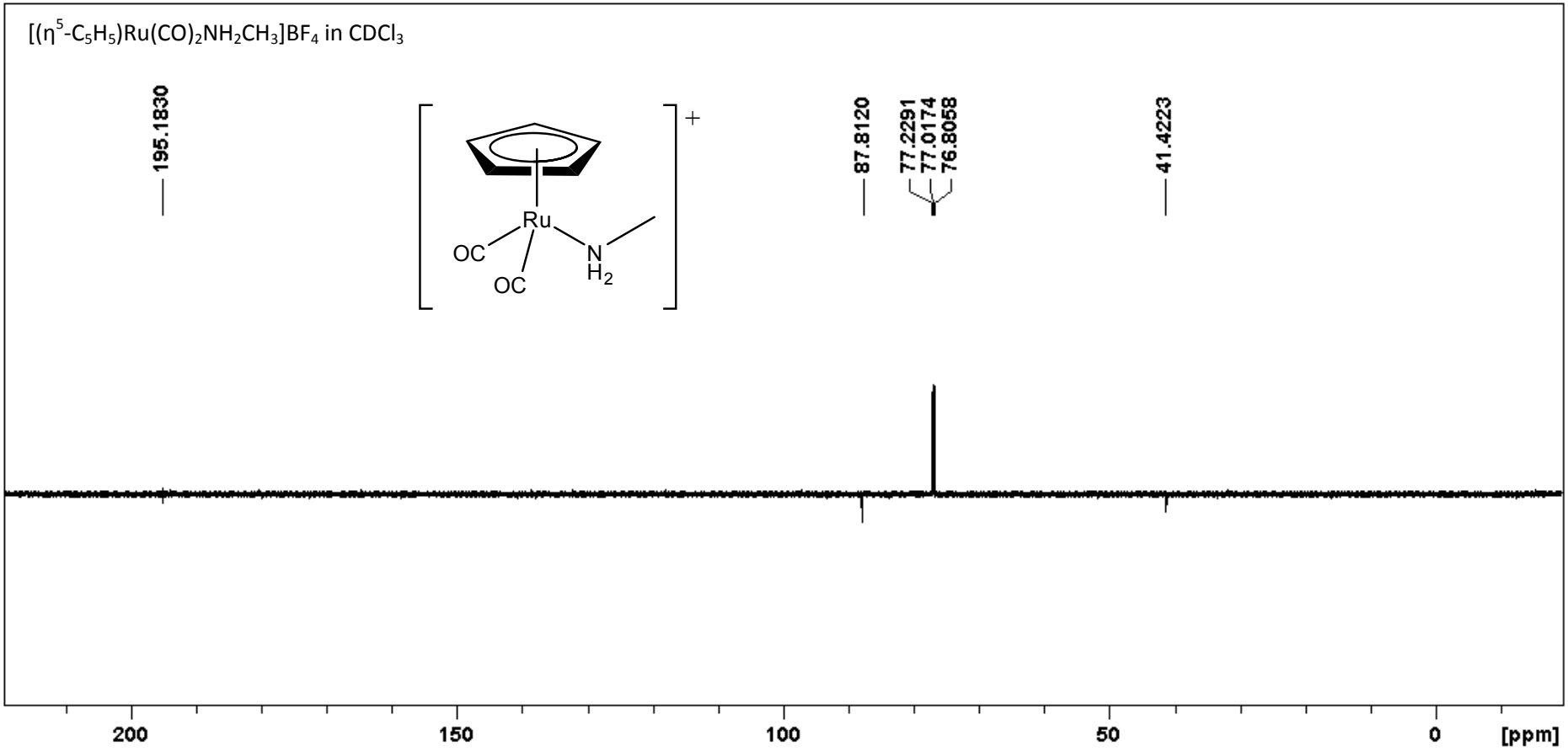
[(η5-C5H5)Ru(CO)2NH2CH3]BF4 in CDCl3
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N
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+
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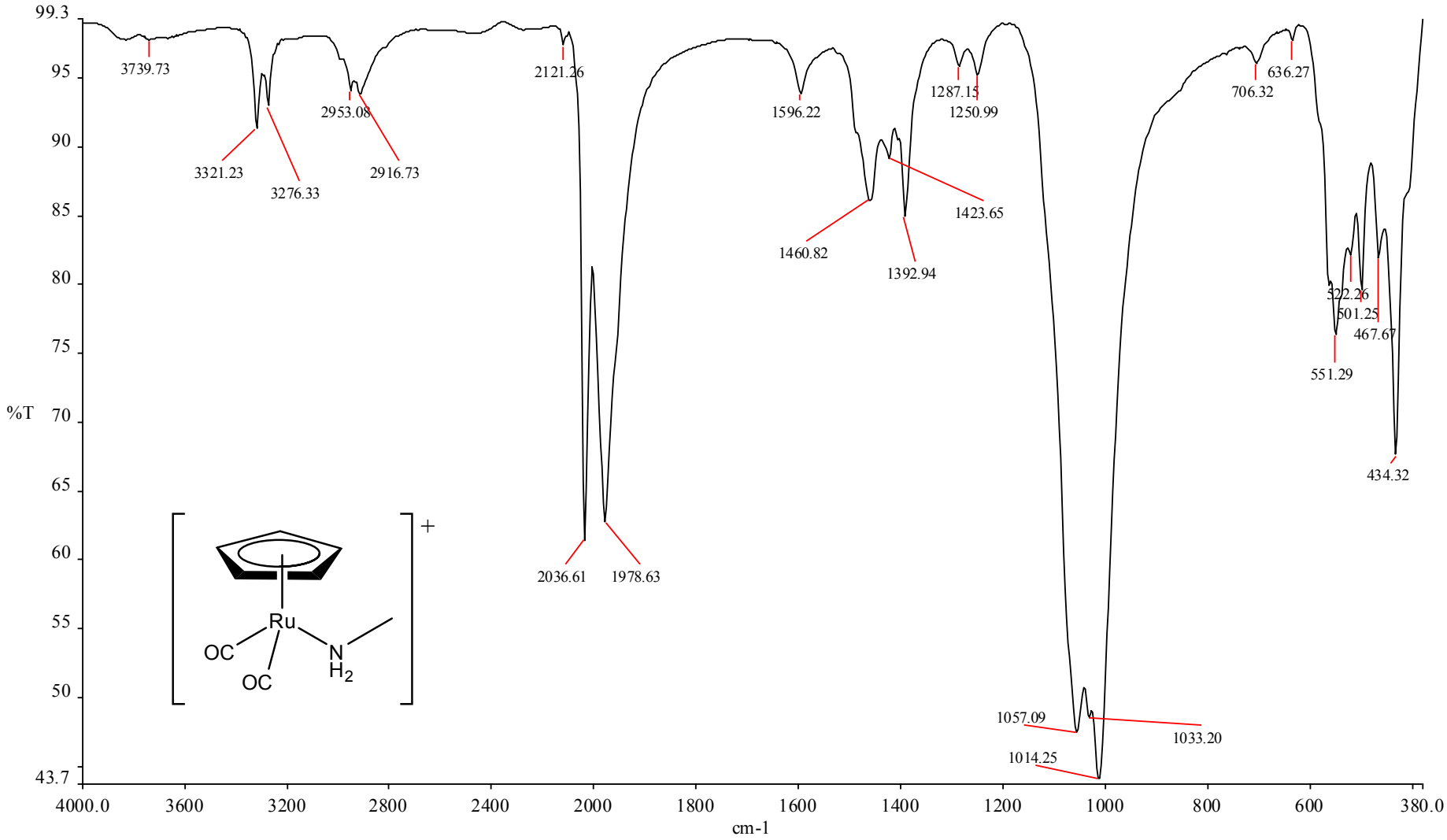
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95
90
85
80
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70
65
60
55
50
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%T
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2953.08
2916.73
2121.26
2036.61
1978.63
1596.22
1460.82
1392.94
1423.65
1287.15
1250.99
1057.09
1033.20
1014.25
706.32
636.27
551.29
522.26
501.25
467.67
434.32
Ru
OC
OC
N
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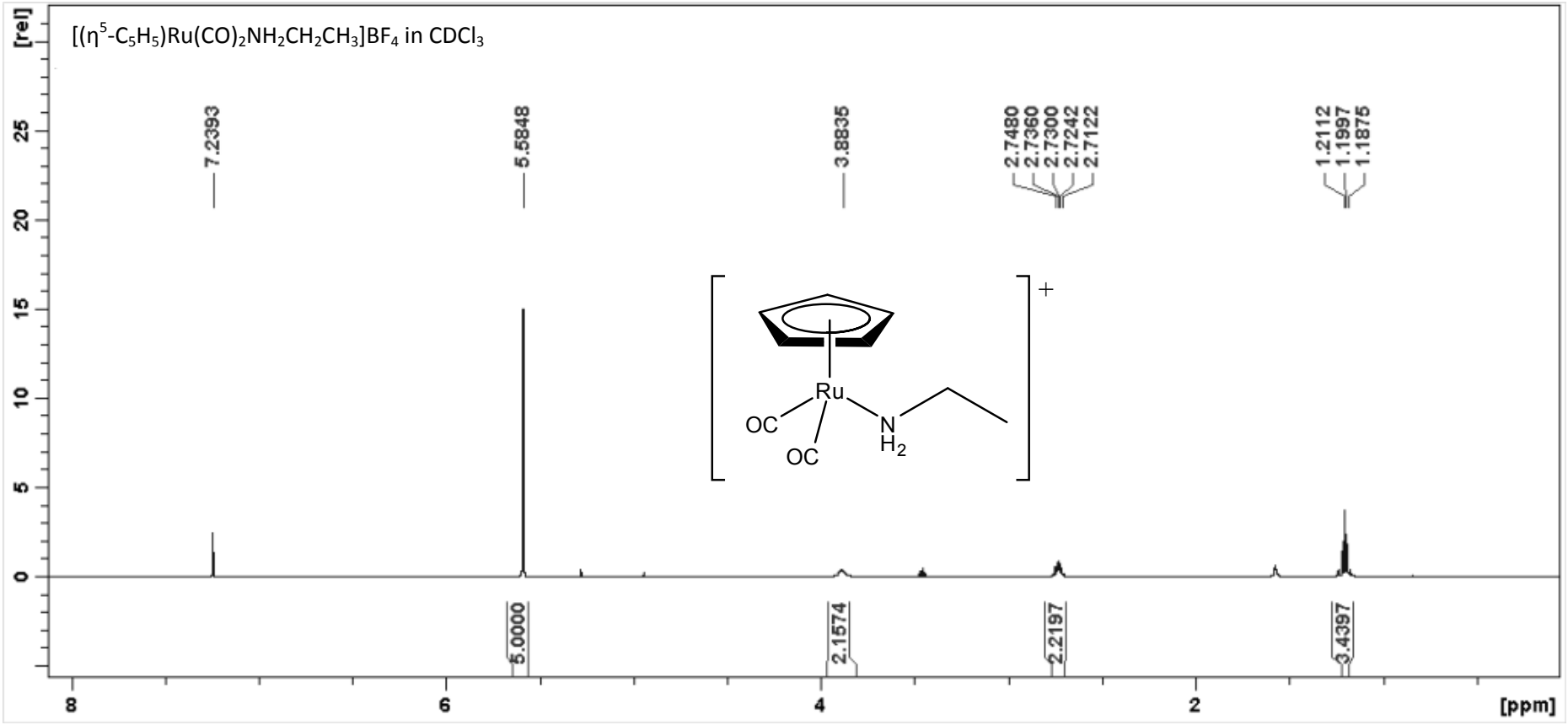
cm-1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20
15
10
5
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2.7300
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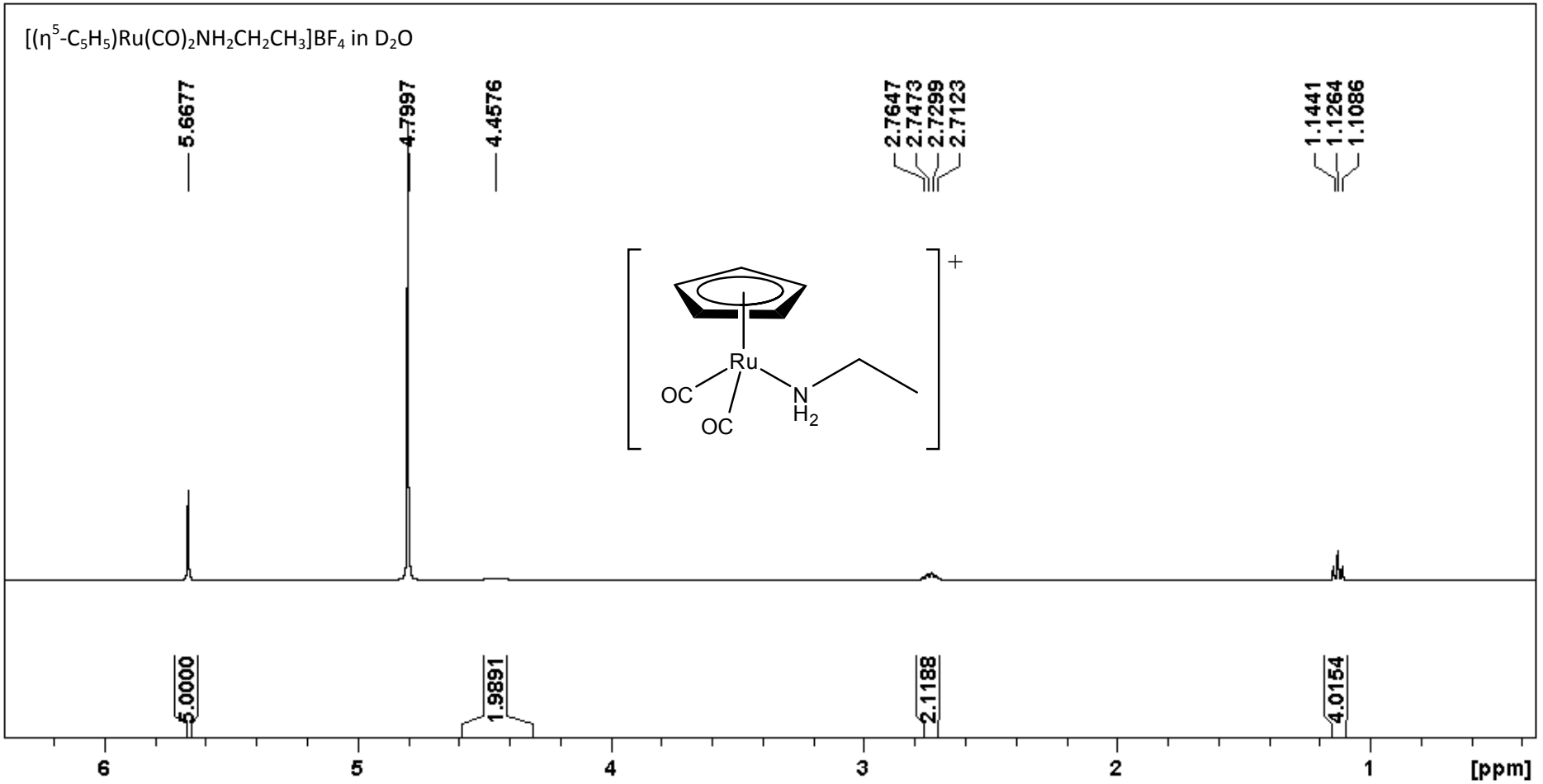
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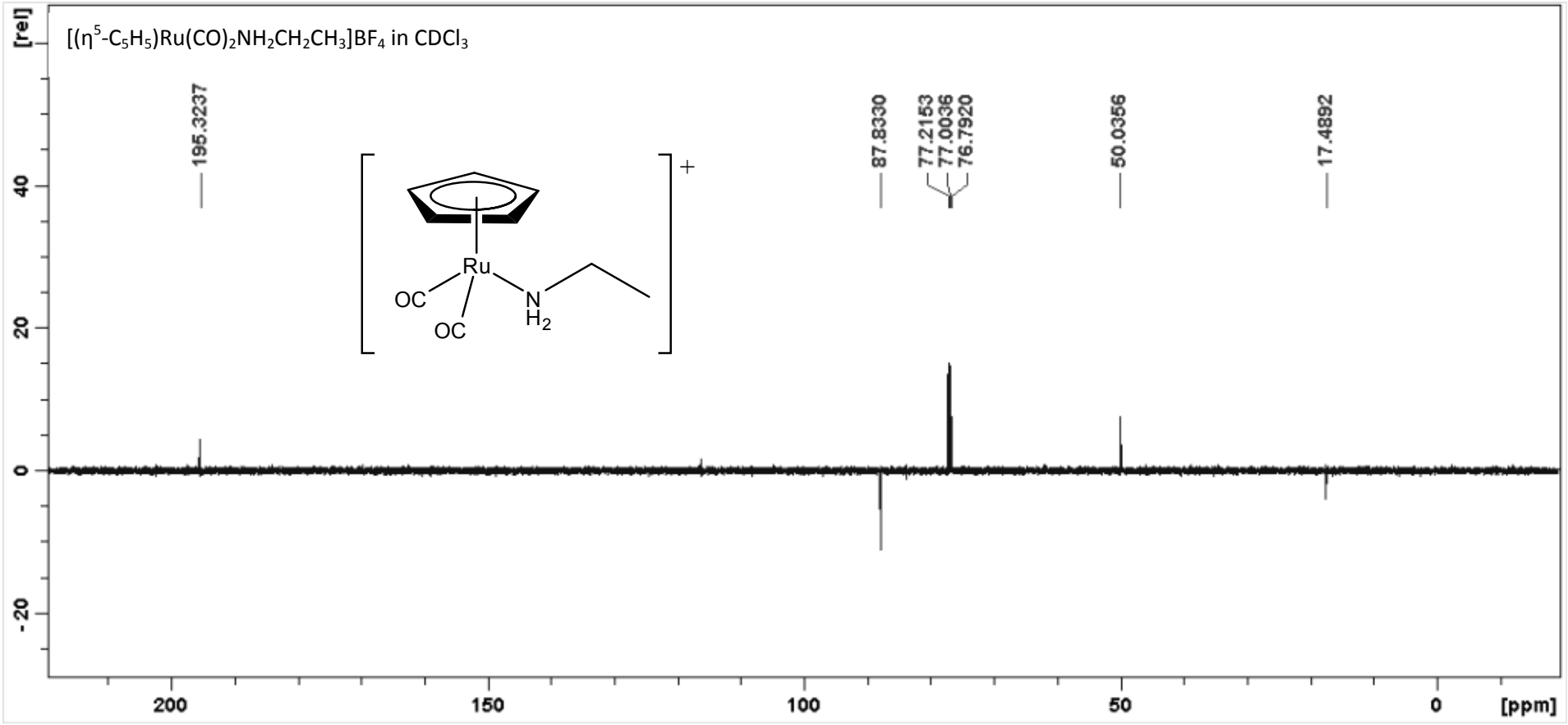
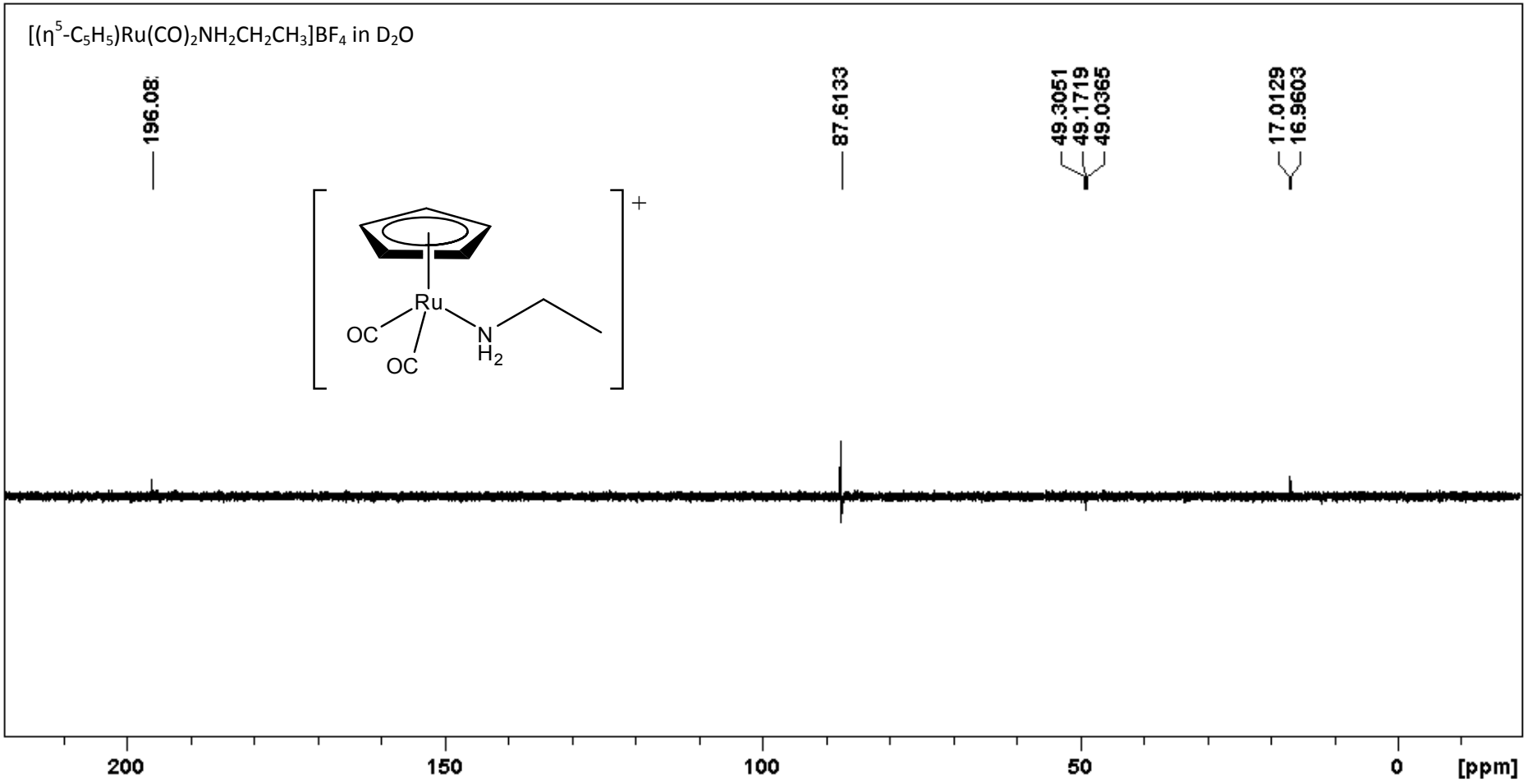
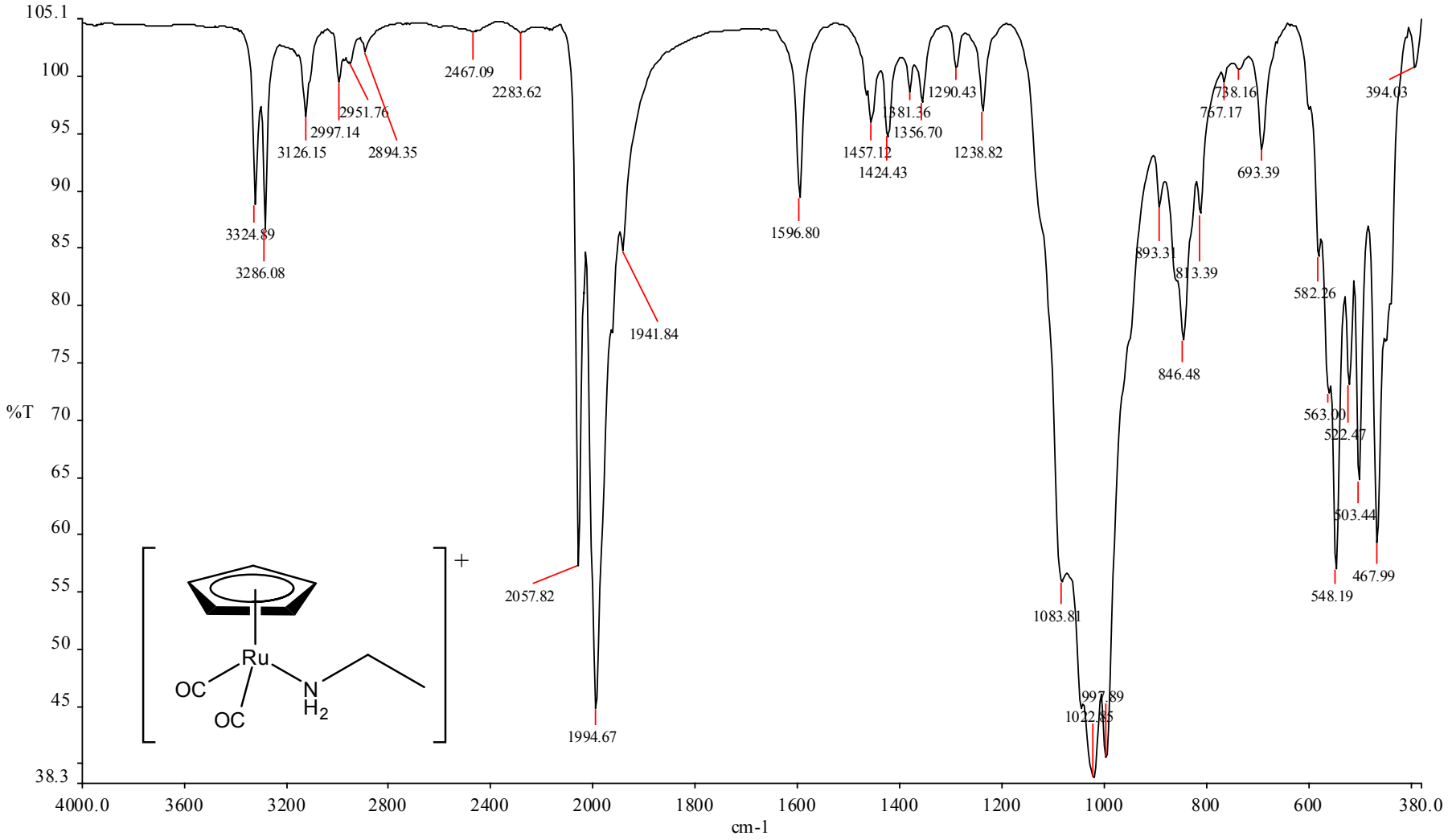
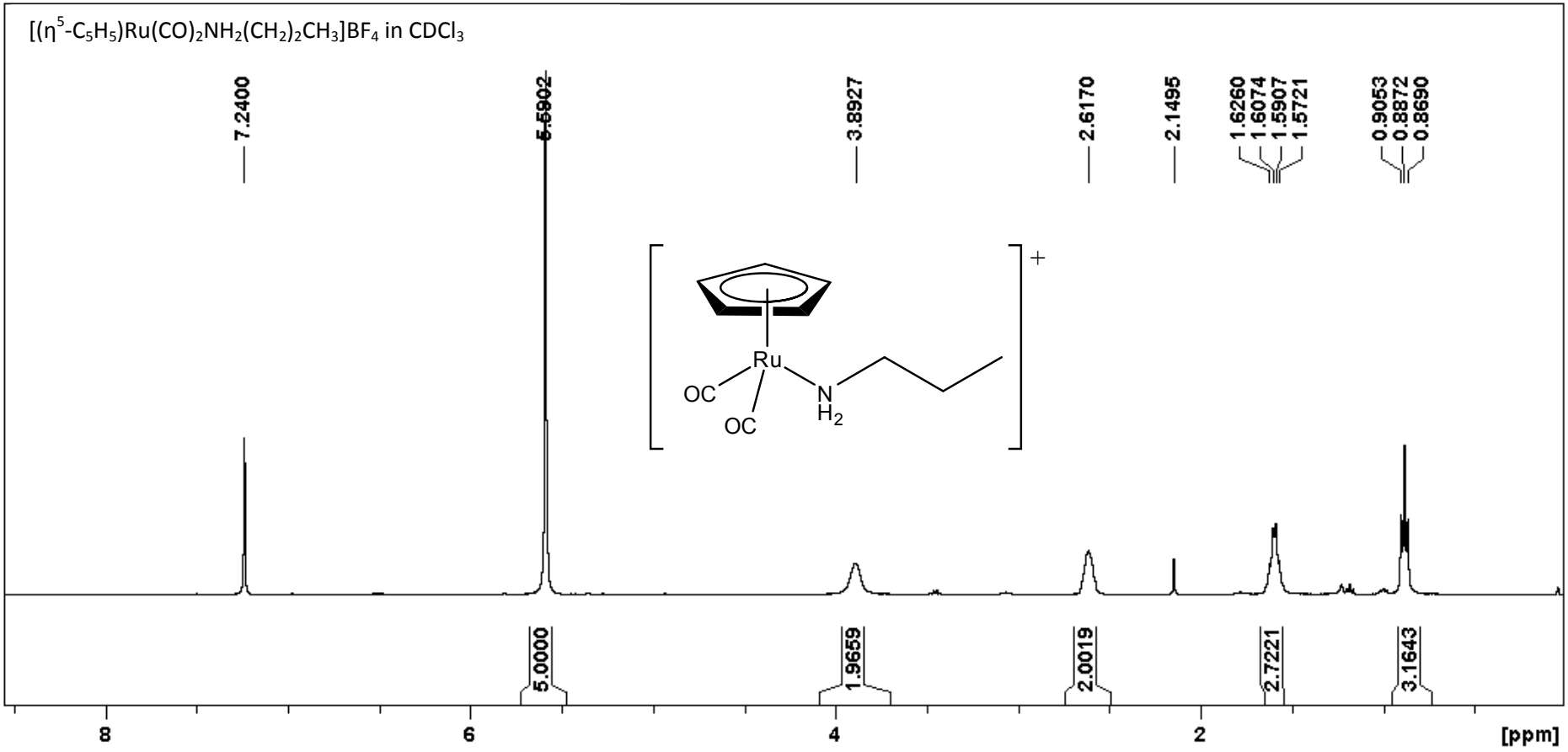
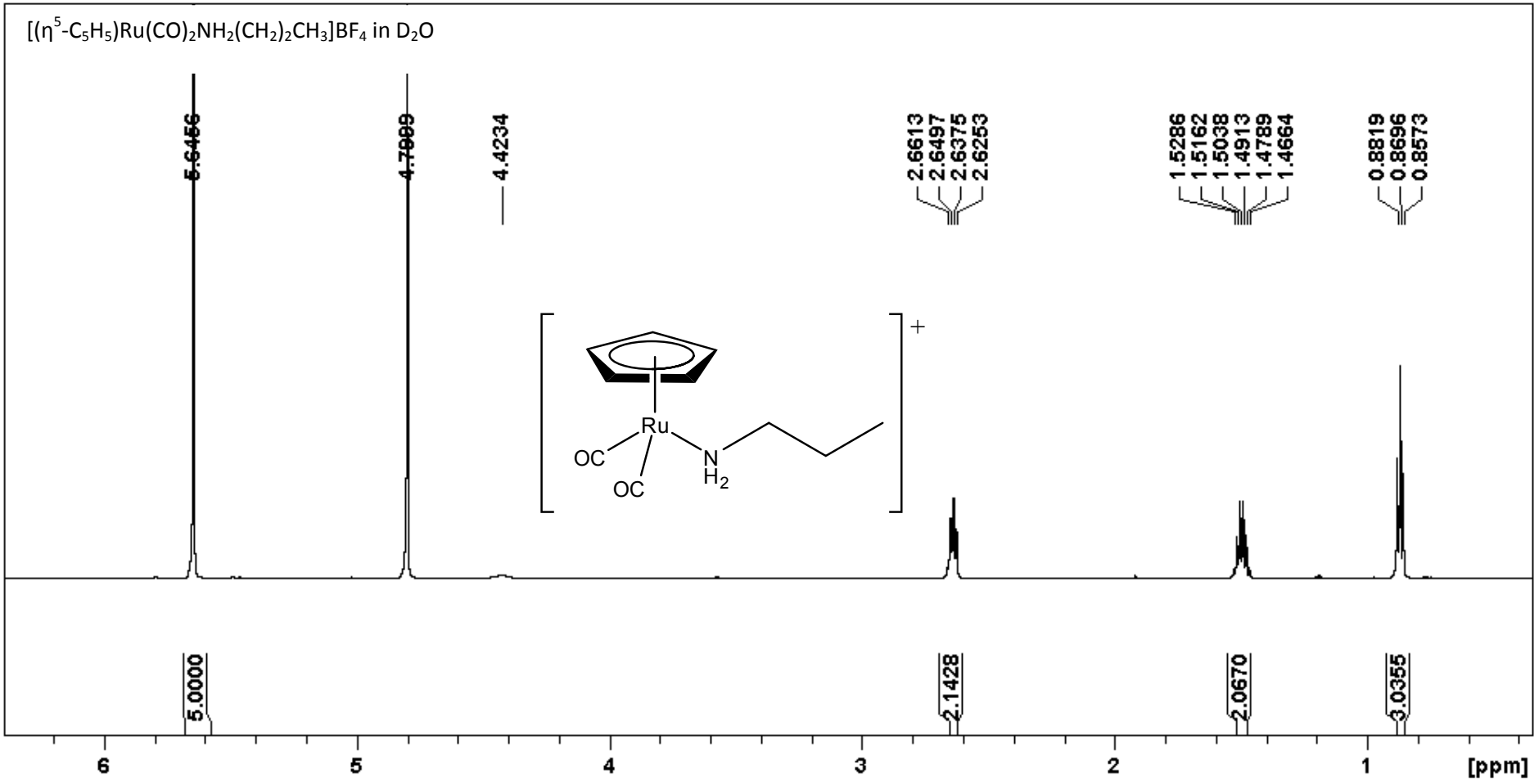
2.7123
1.1441
1.1264
1.1086
Ru
OC
OC
N
H2
+
5.0000
1.9891
2.1188
4.0154
6
5
4
3
2
1
[ppm]

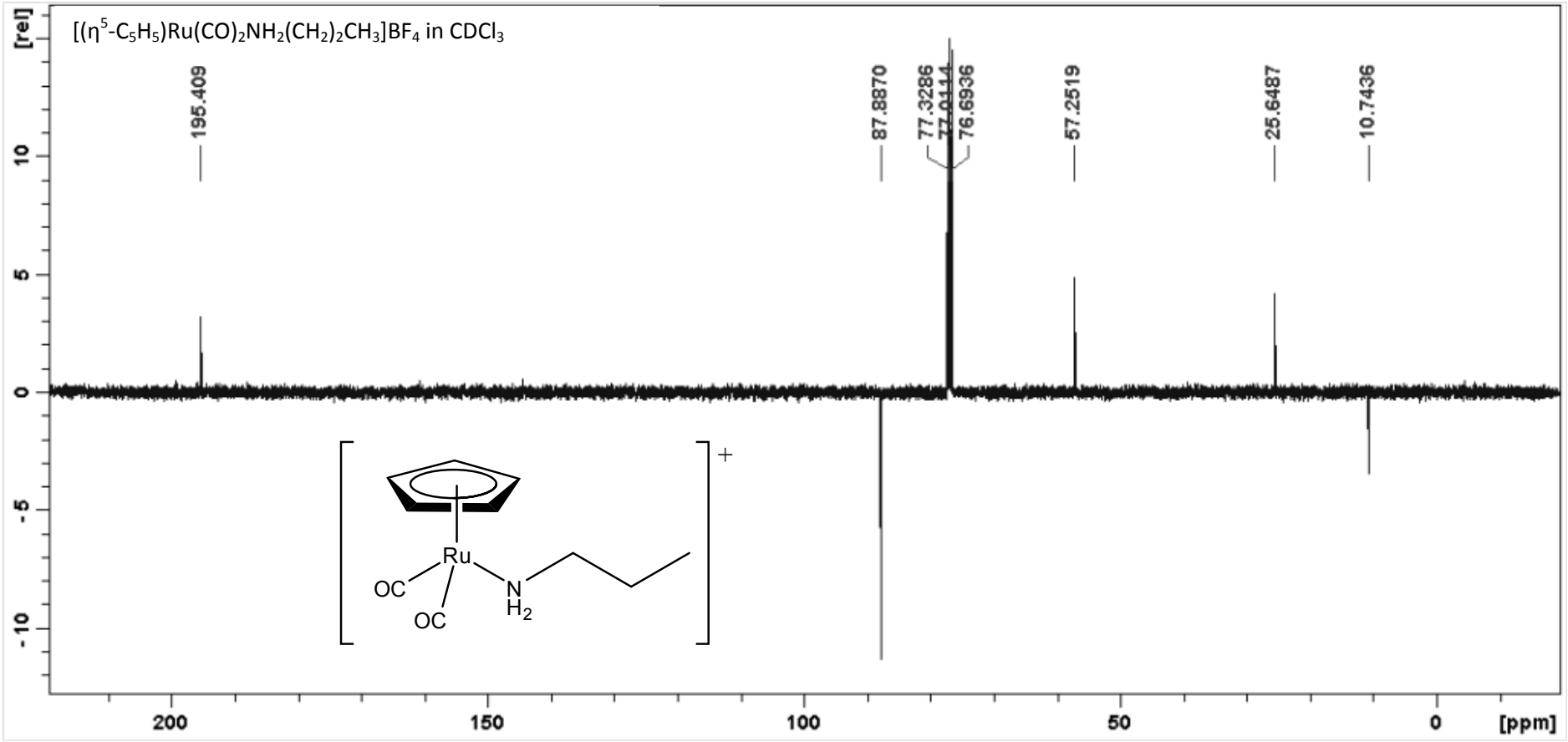

[(η5-C5H5)Ru(CO)2NH2CH2CH3]BF4 in CDCl3
[rel]
195.3237
87.8330
77.2153
77.0036
76.7920
50.0356
17.4892
Ru
OC
OC
N
H2
+
40
20
0
-20
200
150
100
50
0
[ppm]

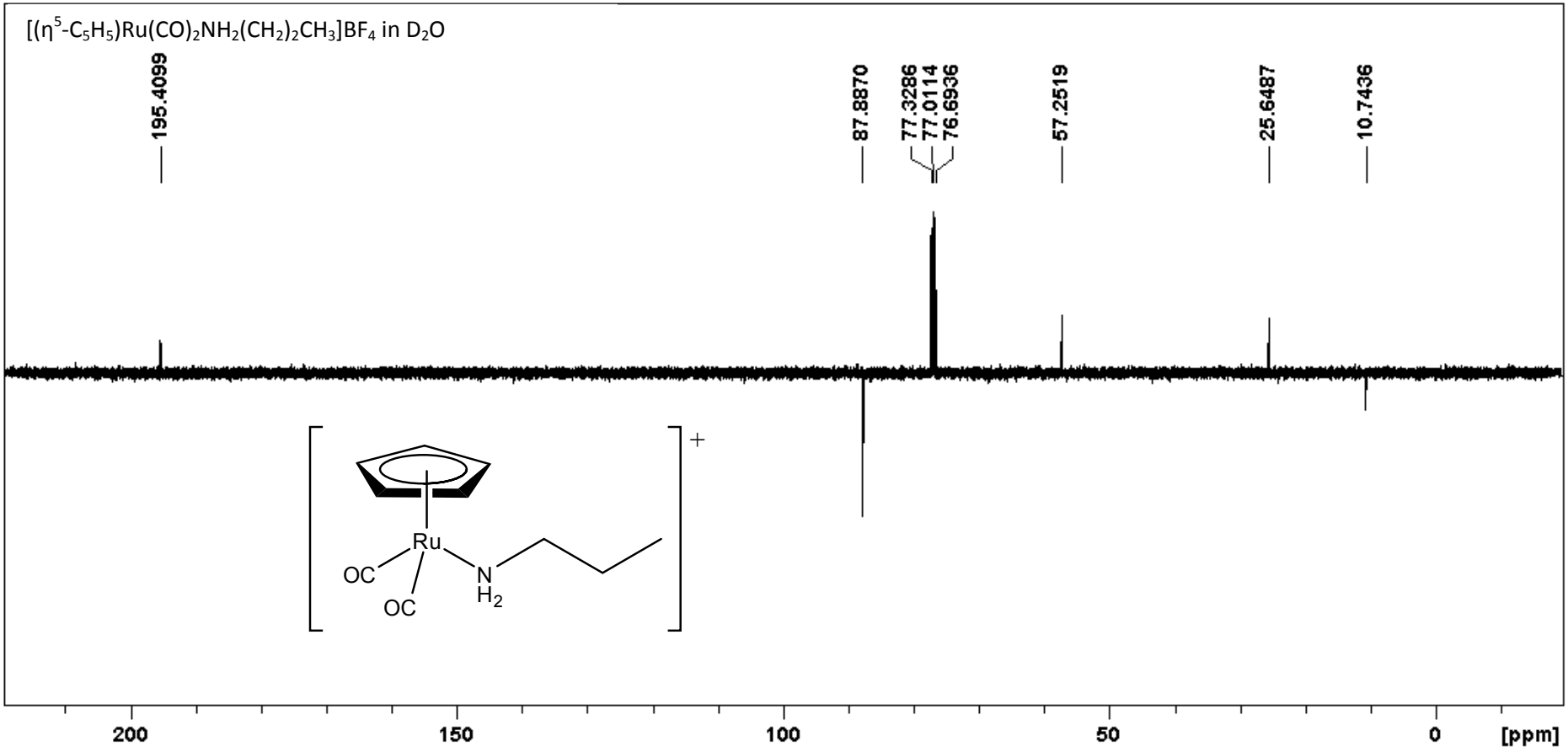

[(η5-C5H5)Ru(CO)2NH2CH2CH3]BF4 in D2O
196.08
87.6133
49.3051
49.1719
49.0365
17.0129
16.9603
Ru
OC
OC
N
H2
+
200
150
100
50
0
[ppm]

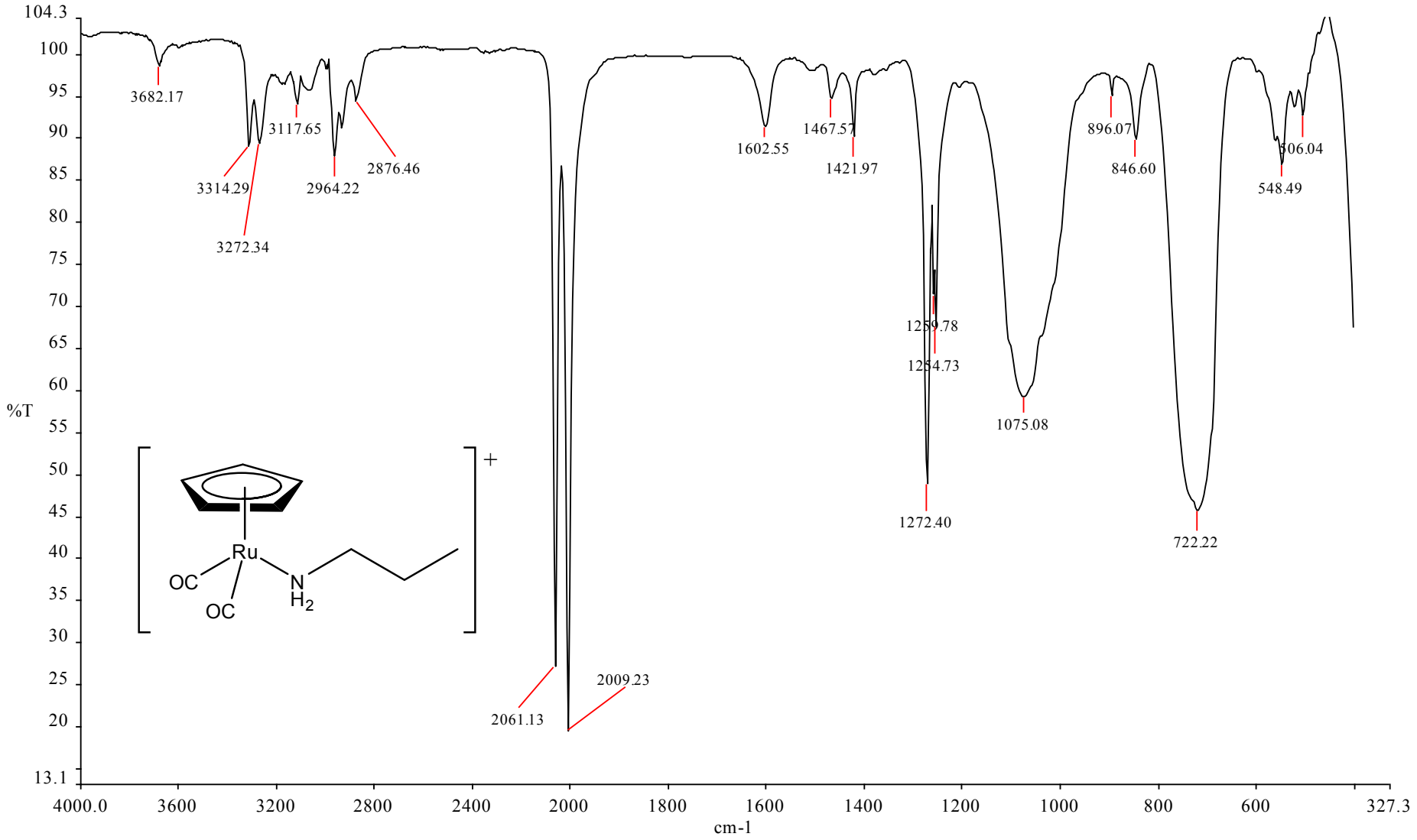

105.1
100
95
90
85
80
75
70
65
60
55
50
45
38.3
%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
380.0
cm-1
3324.89
3286.08
3126.15
2997.14
2951.76
2894.35
2467.09
2283.62
2057.82
1994.67
1941.84
1596.80
1457.12
1424.43
1381.36
1356.70
1290.43
1238.82
1083.81
1022.85
997.89
893.31
846.48
813.39
767.17
738.16
693.39
582.26
563.00
522.47
503.44
548.19
467.99
394.03
Ru
OC
OC
N
H2
+

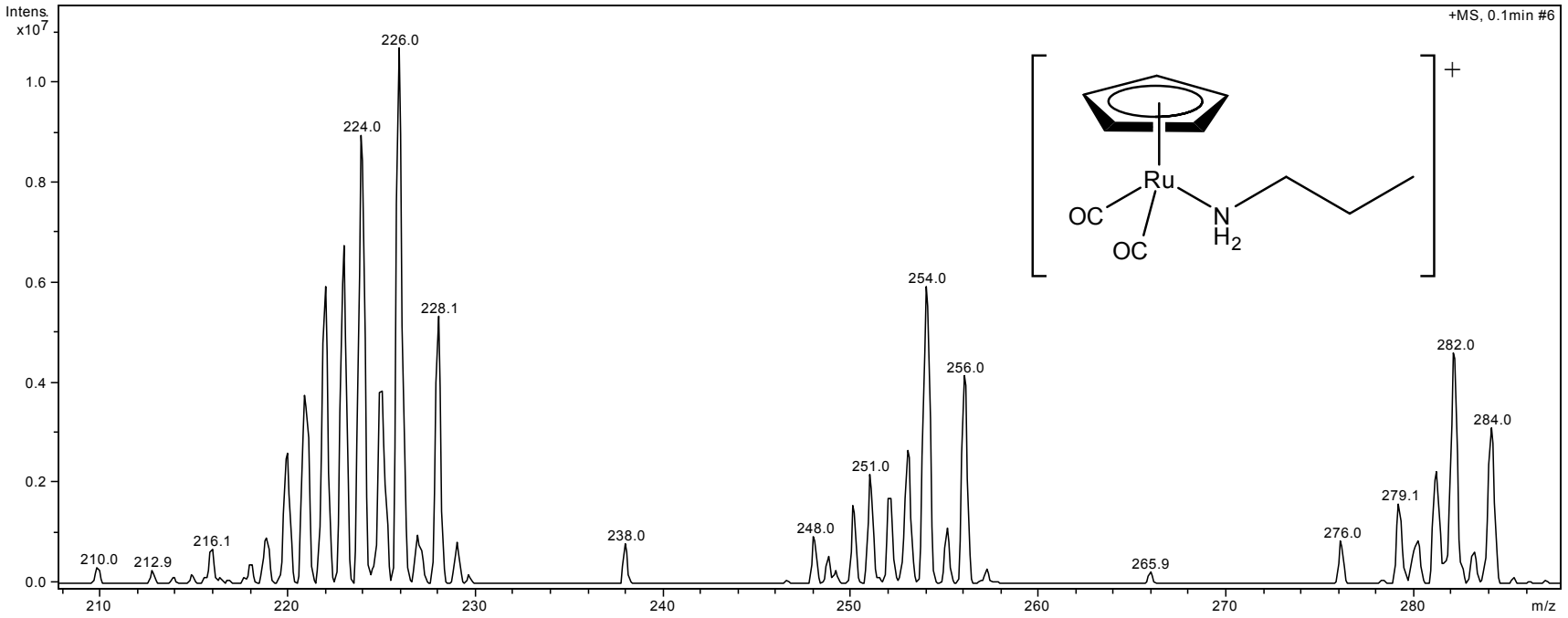

[(η5-C5H5)Ru(CO)2NH2(CH2)2CH3]BF4 in CDCl3
7.2400
5.5902
3.8927
2.6170
2.1495
1.6260
1.6074
1.5907
1.5721
0.9053
0.8872
0.8690
Ru
OC
OC
N
H2
+
5.0000
1.9659
2.0019
2.7221
3.1643
8
6
4
2
[ppm]


[(η5-C5H5)Ru(CO)2NH2(CH2)2CH3]BF4 in D2O
5.6456
4.7099
4.4234
2.6613
2.6497
2.6375
2.6253
1.5286
1.5162
1.5038
1.4913
1.4789
1.4664
0.8819
0.8696
0.8573
Ru
OC
OC
N
H2
+
5.0000
2.1428
2.0670
3.0355
6
5
4
3
2
1
[ppm]

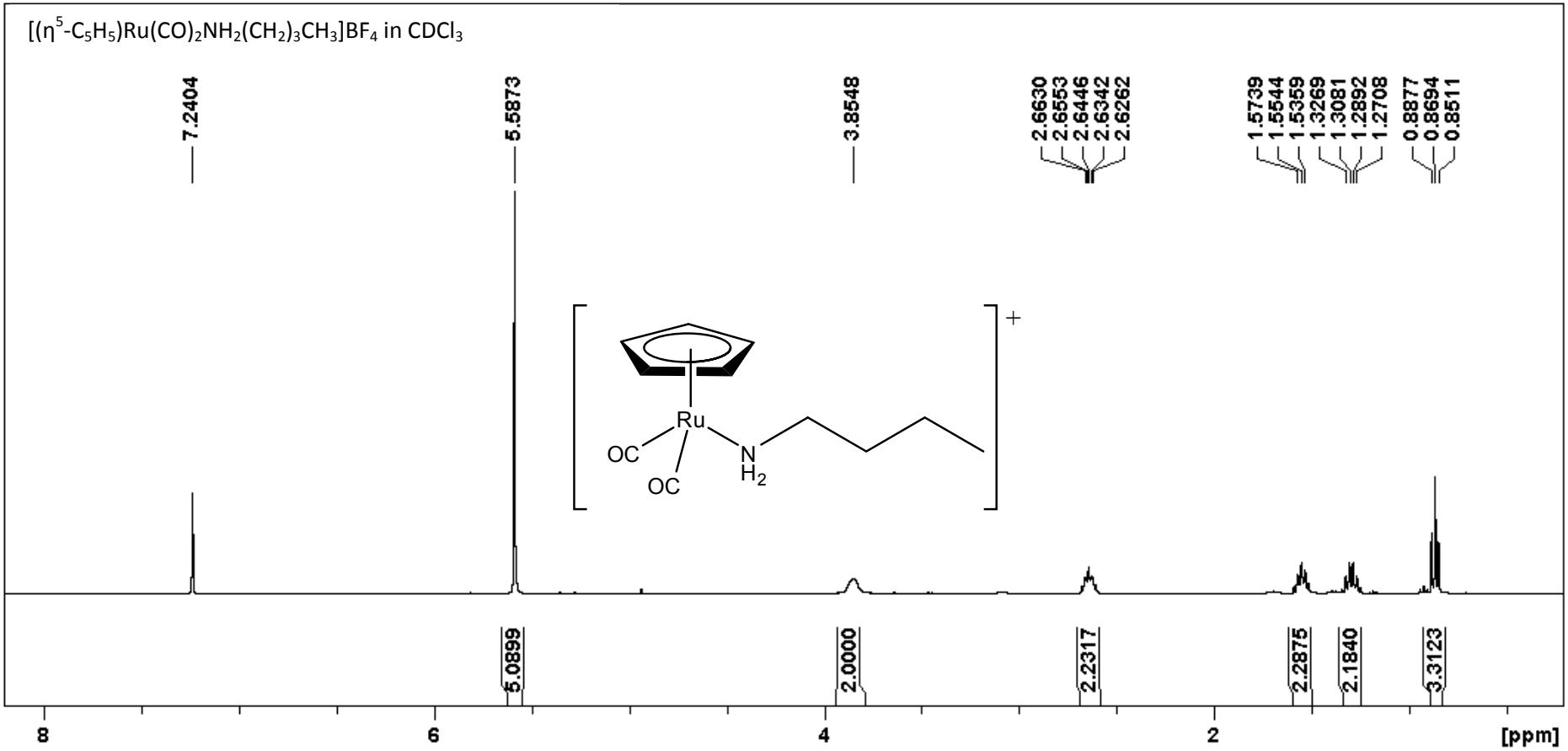

[(η5-C5H5)Ru(CO)2NH2(CH2)2CH3]BF4 in CDCl3
195.409
87.8870
77.3286
77.0114
76.6936
57.2519
25.6487
10.7436
[rel]
10
5
0
-5
-10
200
150
100
50
0
[ppm]
Ru
OC
OC
N
H2
+

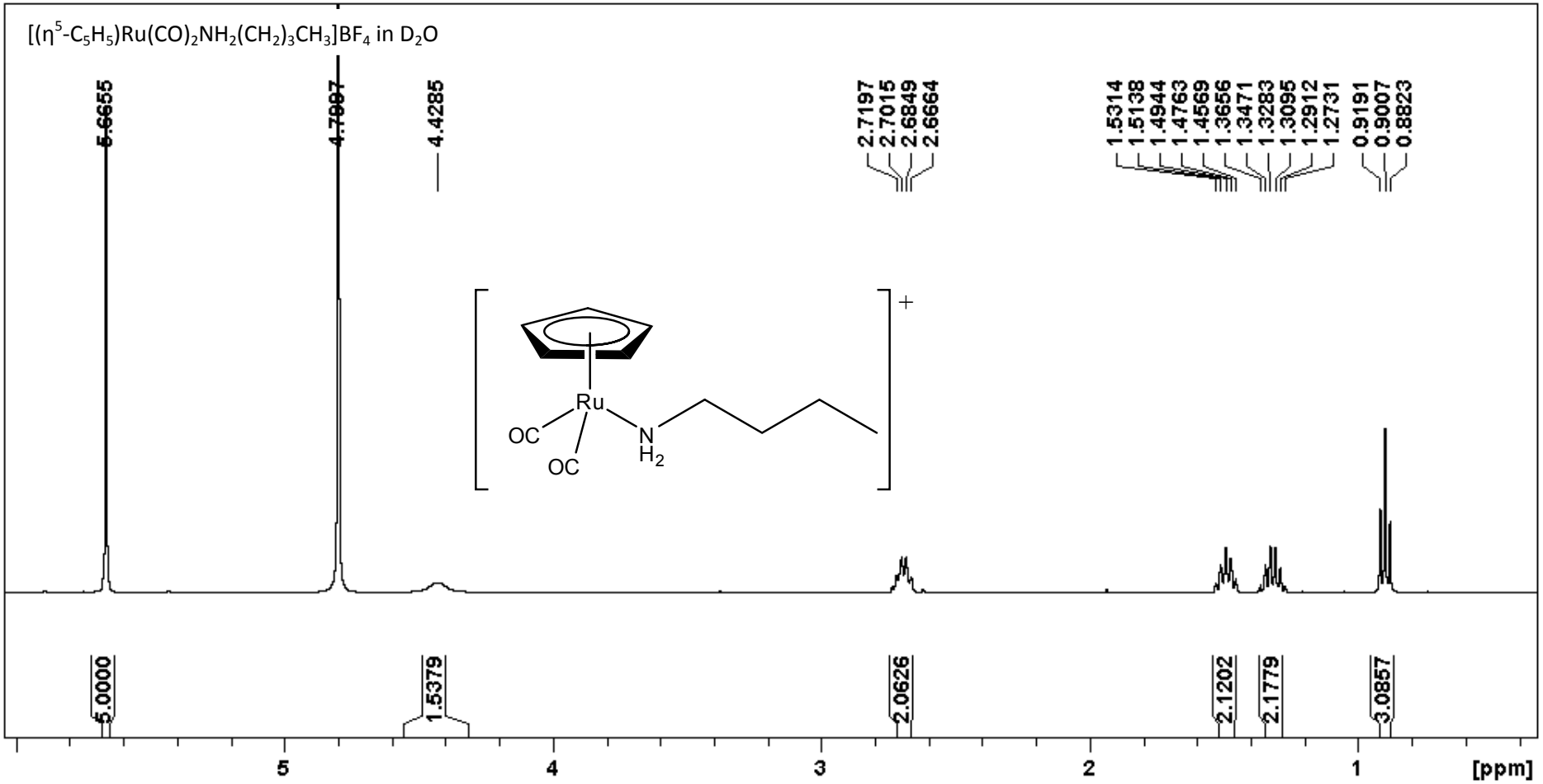

[(η5-C5H5)Ru(CO)2NH2(CH2)2CH3]BF4 in D2O
195.4099
87.8870
77.3286
77.0114
76.6936
57.2519
25.6487
10.7436
Ru
OC
OC
N
H2
+
200
150
100
50
0
[ppm]

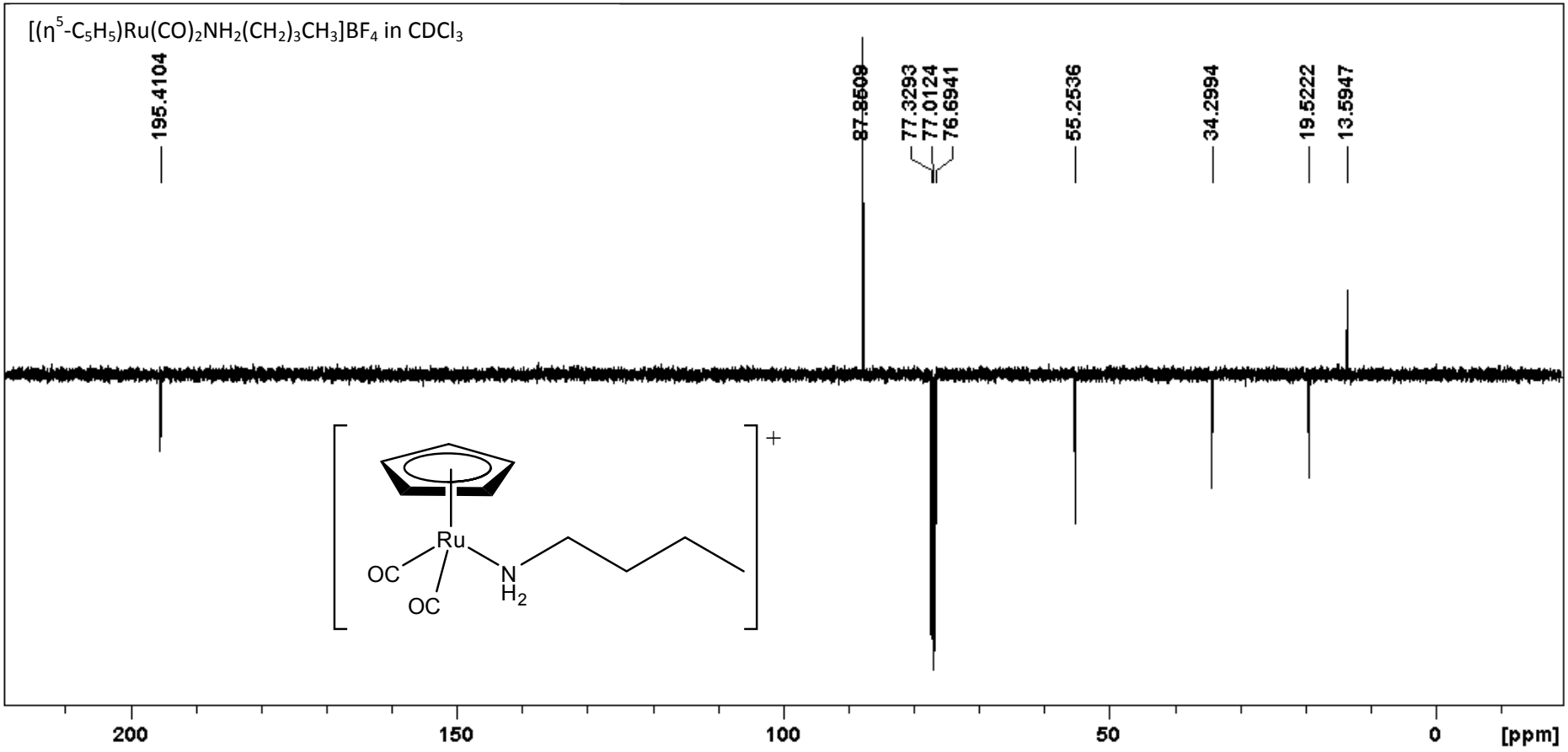

104.3
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
13.1
%T
3682.17
3314.29
3272.34
3117.65
2964.22
2876.46
2061.13
2009.23
1602.55
1467.57
1421.97
1272.40
1259.78
1254.73
1075.08
896.07
846.60
722.22
606.04
548.49
Ru
OC
OC
N
H2
+
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
327.3
cm-1

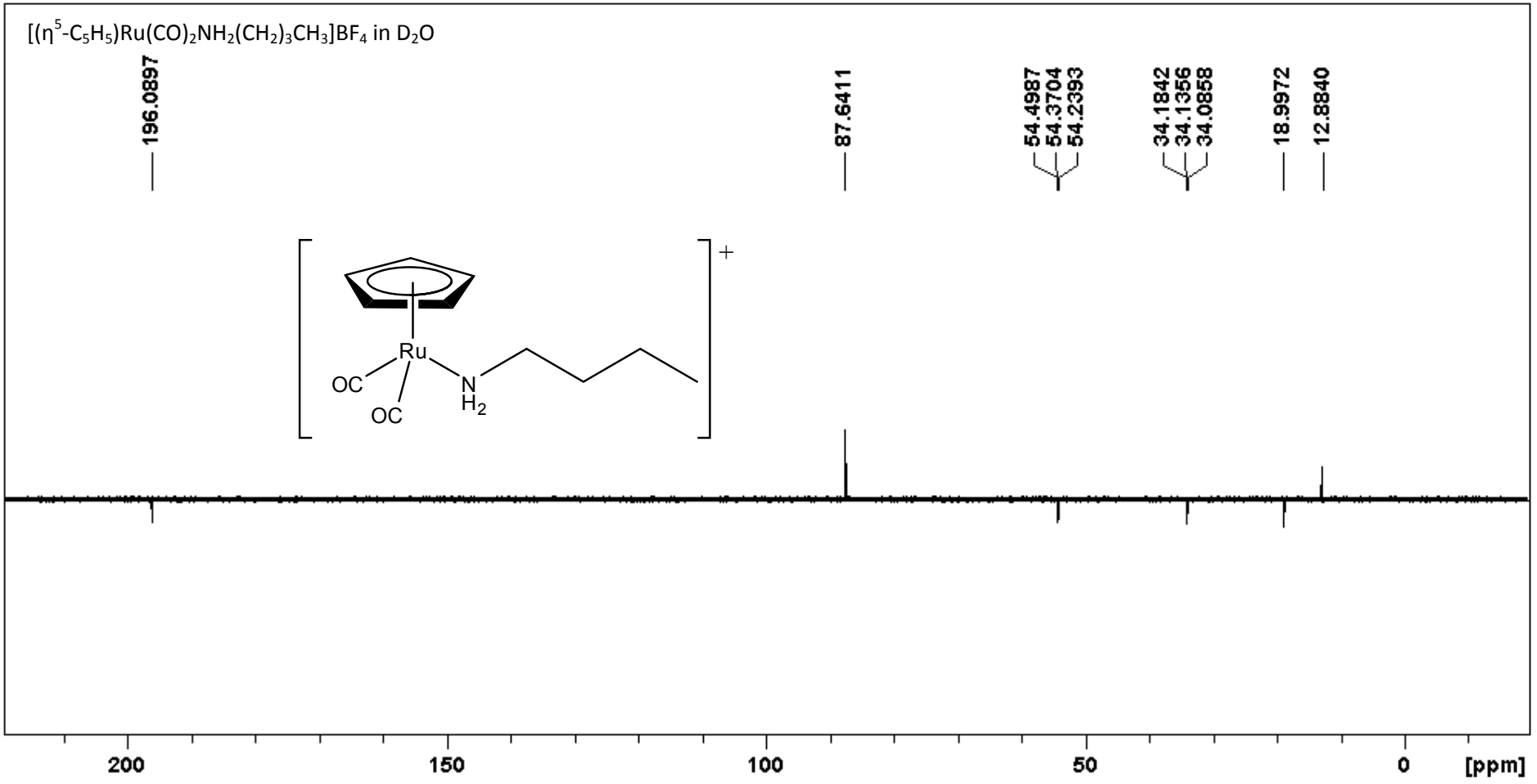


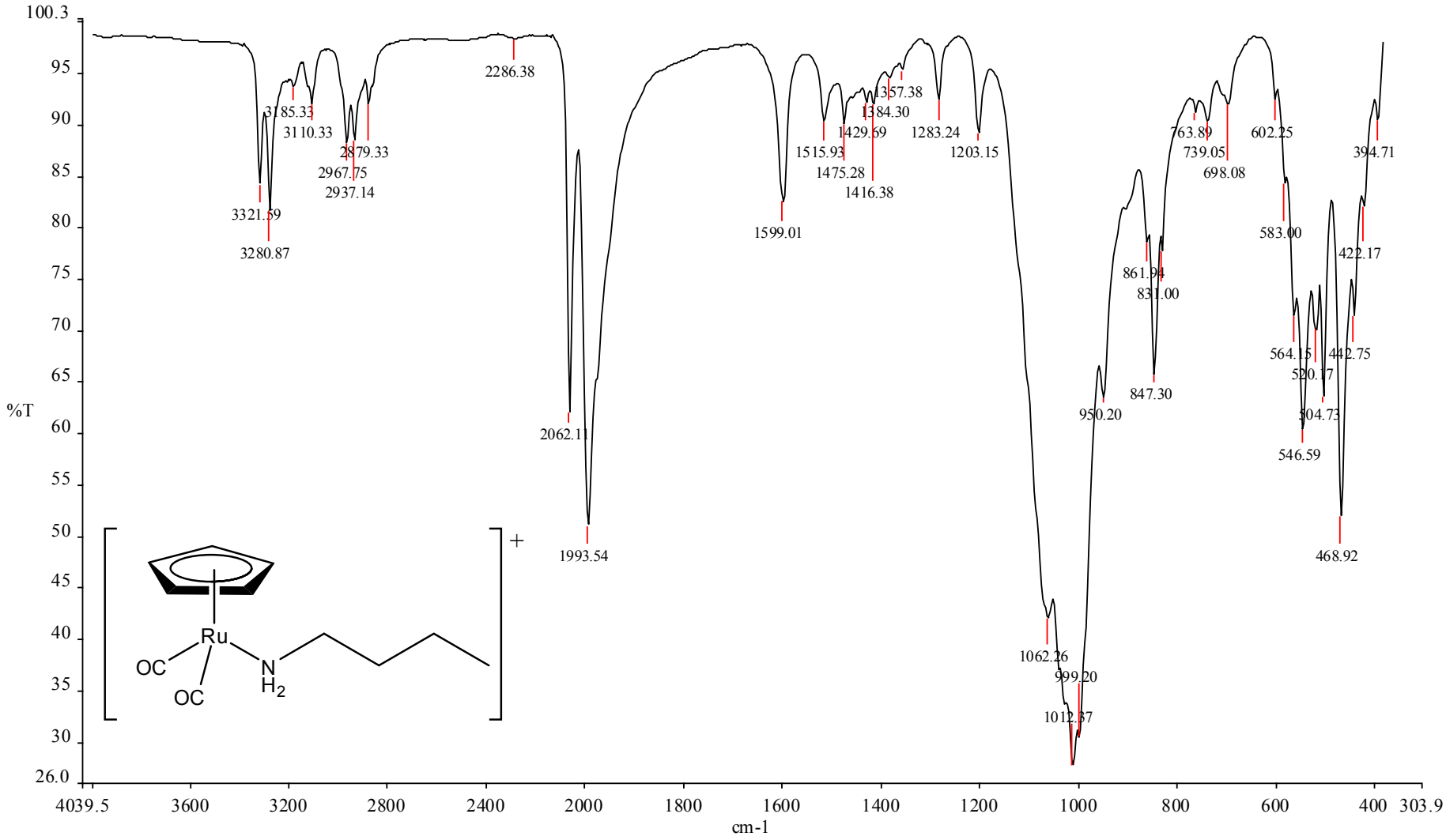

$[CpRuNH_2C_3H_7]^+$ $[CpRu(CO)NH_2C_3H_7]^+$ $[CpRu(CO)_2NH_2C_3H_7]^+$

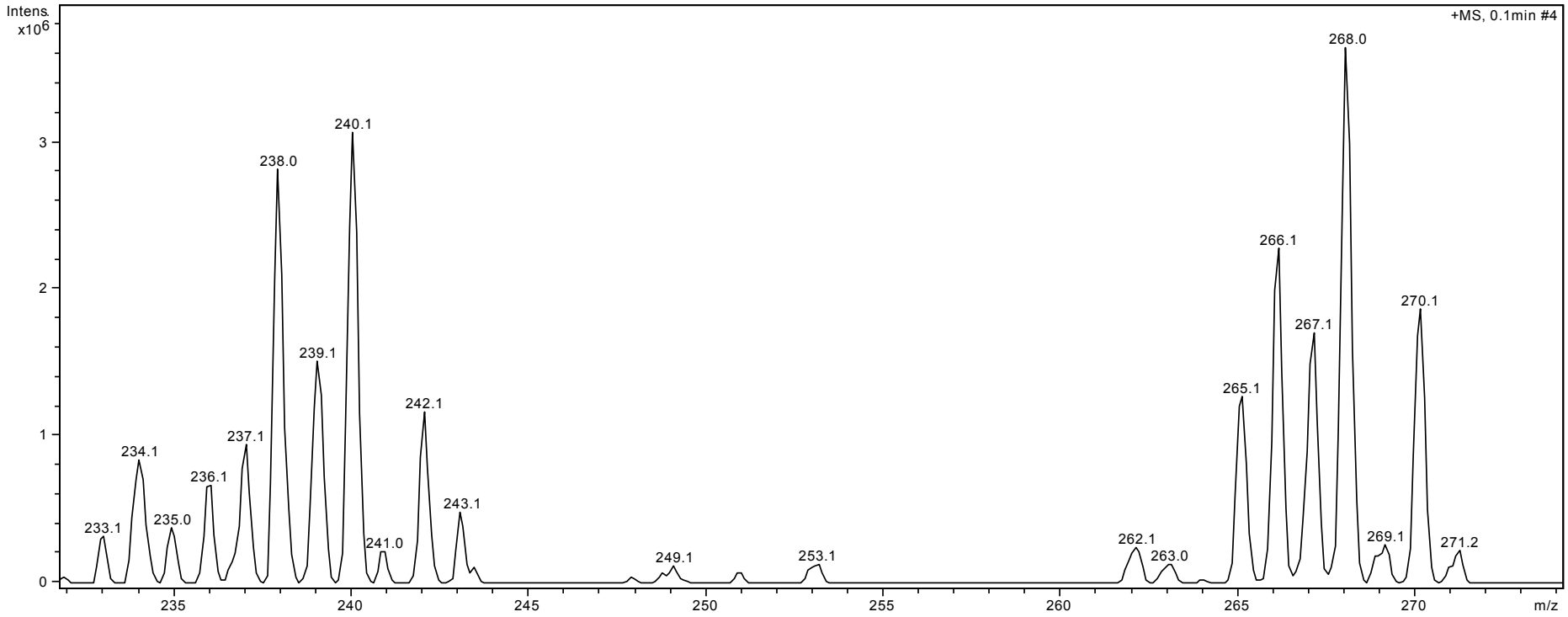

[(η5-C5H5)Ru(CO)2NH2(CH2)3CH3]BF4 in CDCl3
7.2404
5.5873
3.8548
2.6630
2.6553
2.6446
2.6342
2.6262
1.5739
1.5544
1.5359
1.3269
1.3081
1.2892
1.2708
0.8877
0.8694
0.8511
Ru
OC
OC
N
H2
+
5.0899
2.0000
2.2317
2.2875
2.1840
3.3123
8
6
4
2
[ppm]


[(η5-C5H5)Ru(CO)2NH2(CH2)3CH3]BF4 in D2O
5.6655
4.7987
4.4285
2.7197
2.7015
2.6849
2.6664
1.5314
1.5138
1.4944
1.4763
1.4569
1.3656
1.3471
1.3283
1.3095
1.2912
1.2731
0.9191
0.9007
0.8823
Ru
OC
OC
N
H2
+
5.0000
1.5379
2.0626
2.1202
2.1779
3.0857
5
4
3
2
1
[ppm]

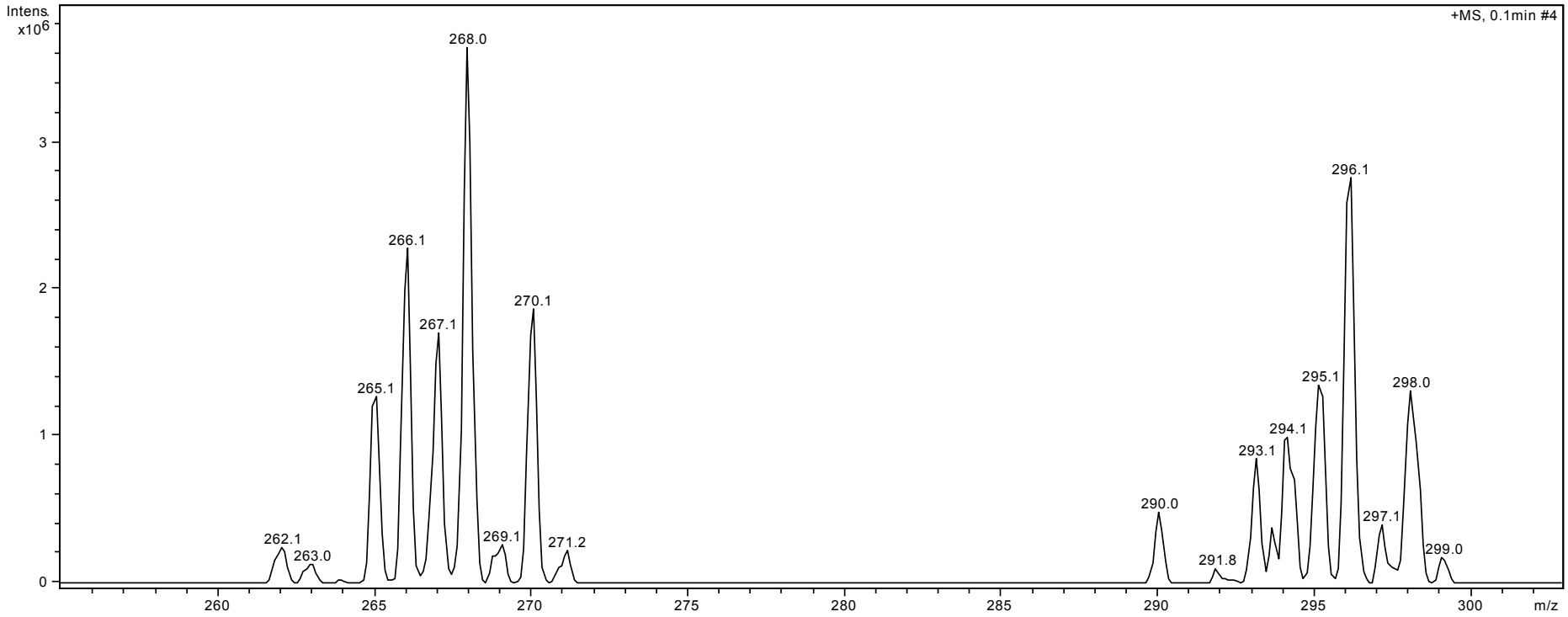

[(η5-C5H5)Ru(CO)2NH2(CH2)3CH3]BF4 in CDCl3
195.4104
87.8509
77.3293
77.0124
76.6941
55.2536
34.2994
19.5222
13.5947
Ru
OC
OC
N
H2
+
200
150
100
50
0
[ppm]


[(η5-C5H5)Ru(CO)2NH2(CH2)3CH3]BF4 in D2O
196.0897
87.6411
54.4987
54.3704
54.2393
34.1842
34.1356
34.0858
18.9972
12.8840
Ru
OC
OC
N
H2
+
200
150
100
50
0
[ppm]


100.3
95
90
85
80
75
70
65
60
55
50
45
40
35
30
26.0
%T
4039.5
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
303.9
cm-1
3321.59
3280.87
3185.33
3110.33
2967.75
2937.14
2879.33
2286.38
2062.11
1993.54
1599.01
1515.93
1475.28
1429.69
1416.38
1384.30
1357.38
1283.24
1203.15
1062.26
1012.87
999.20
950.20
861.94
847.30
831.00
763.89
739.05
698.08
602.25
583.00
564.15
546.59
520.17
504.73
468.92
442.75
422.17
394.71
Ru
OC
OC
N
H2
+

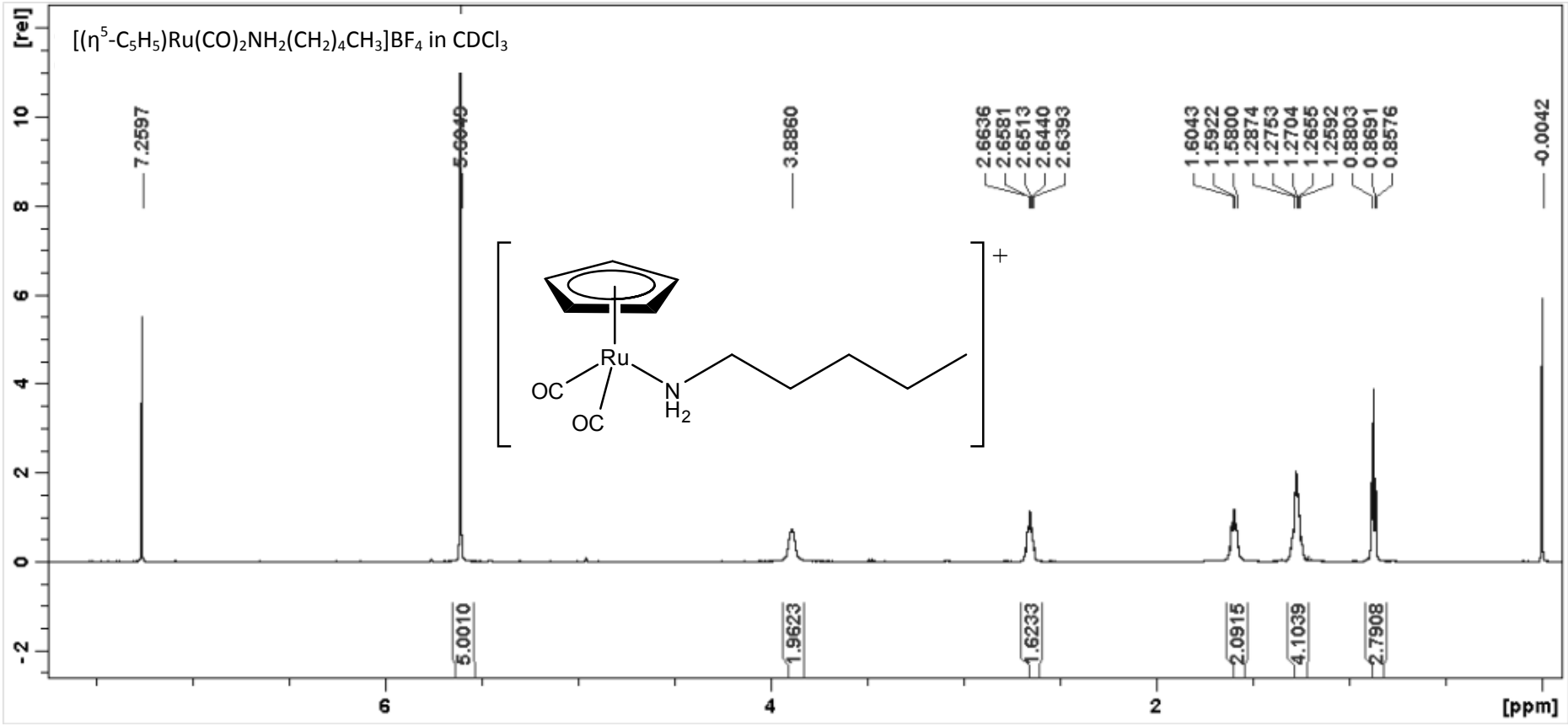


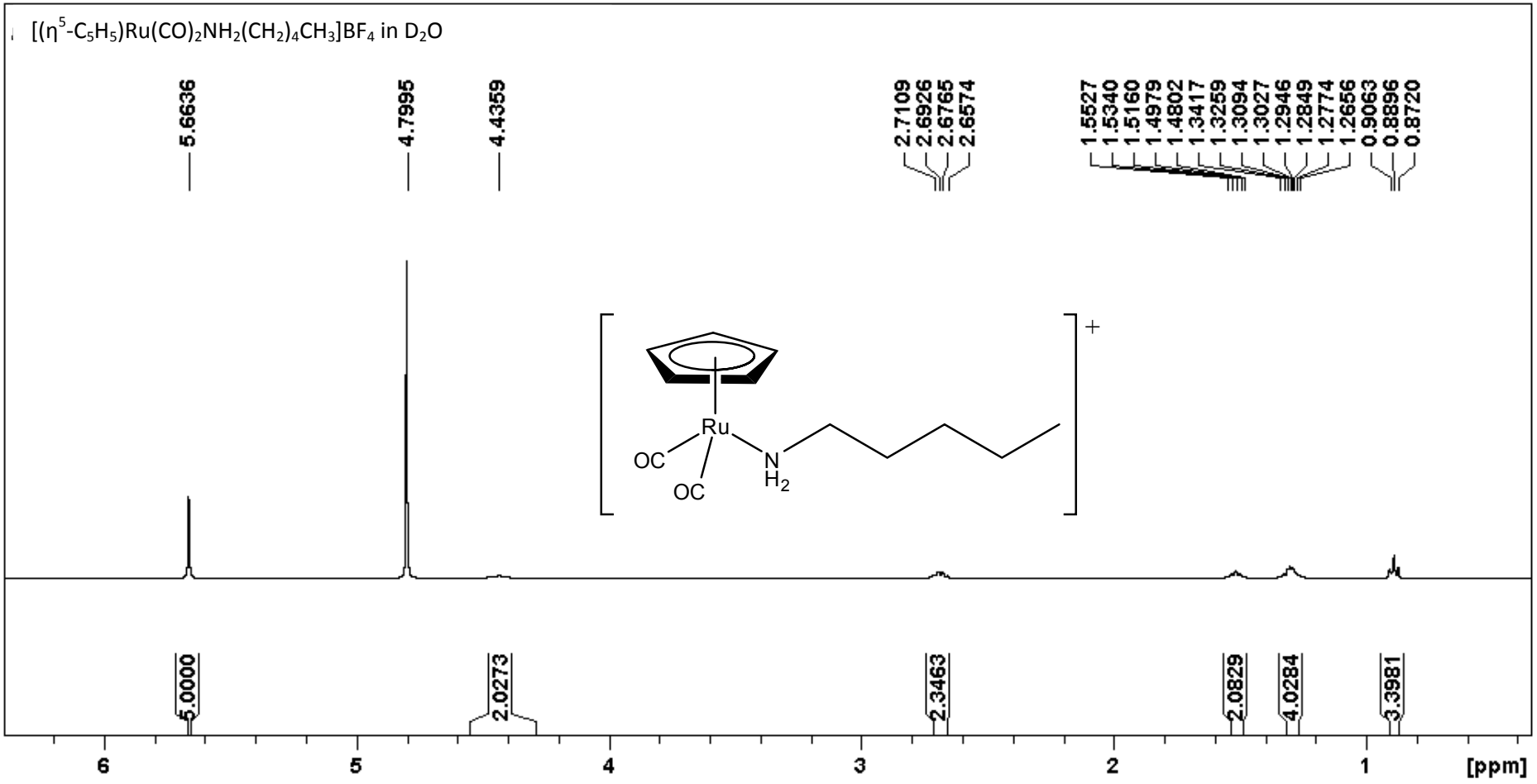

$[CpRuNH_2C_4H_9]^+$ $[CpRuNH_2(CO)C_4H_9]^+$

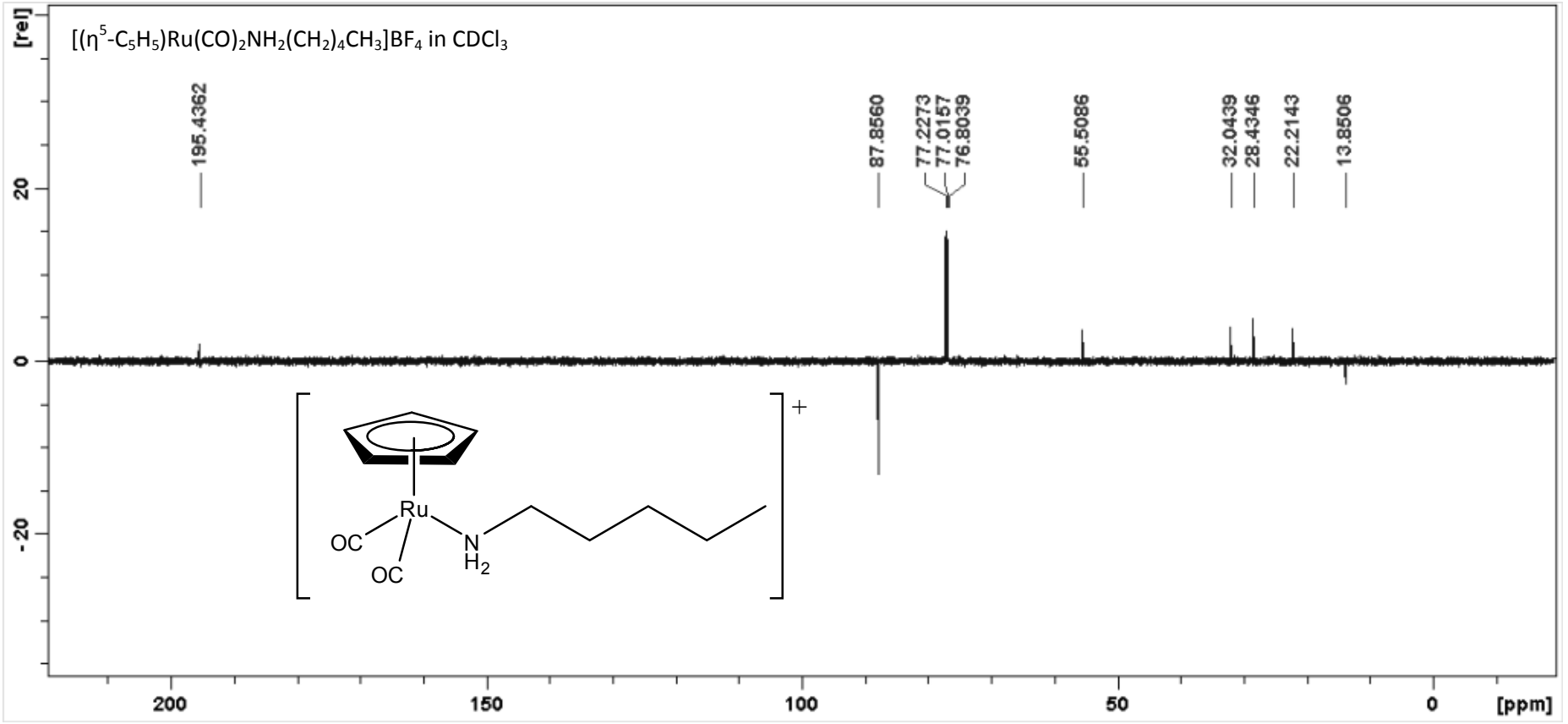


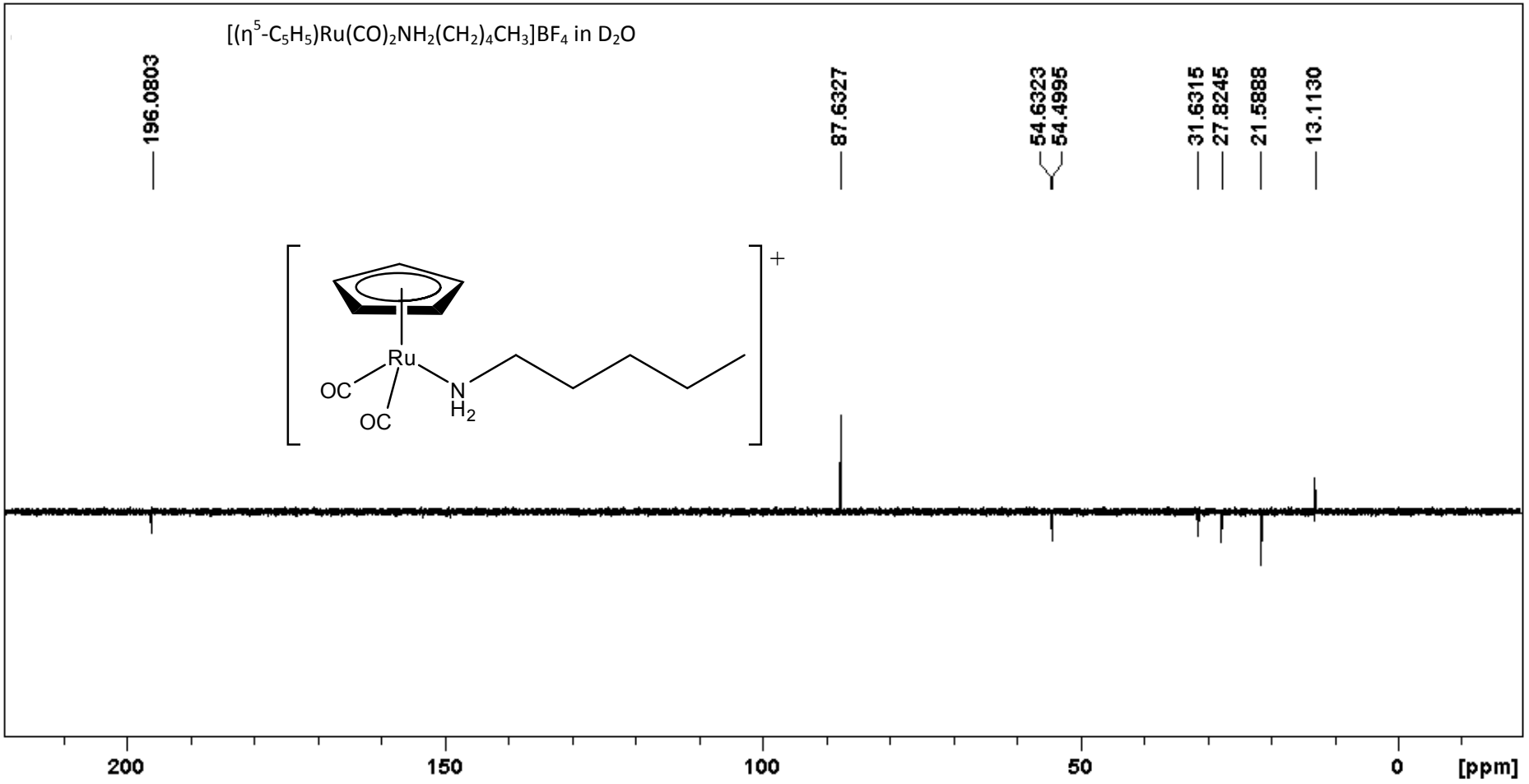

$[CpRuNH_2(CO)C_4H_9]^+$

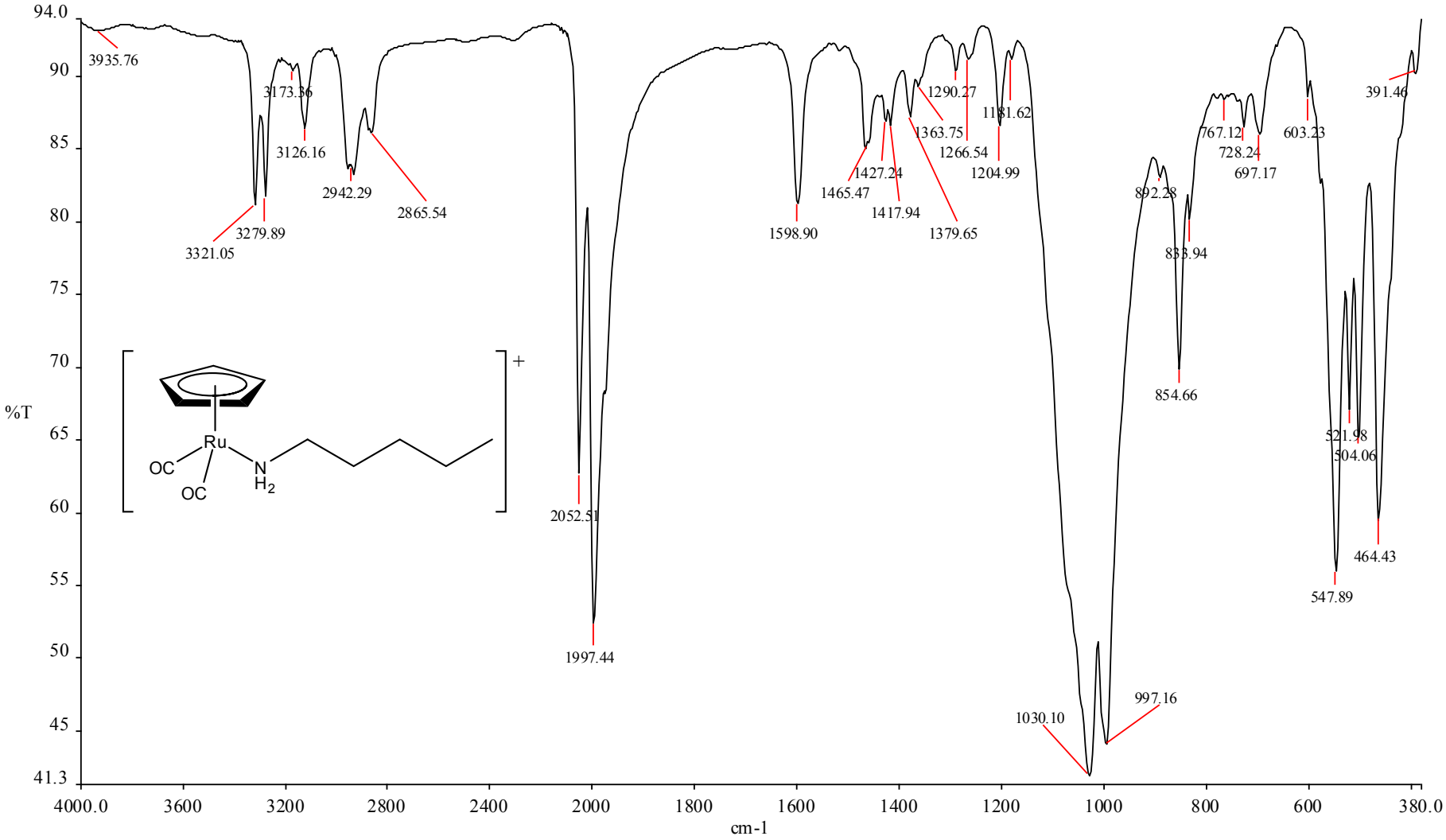
$[CpRuNH_2(CO)_2C_4H_9]^+$

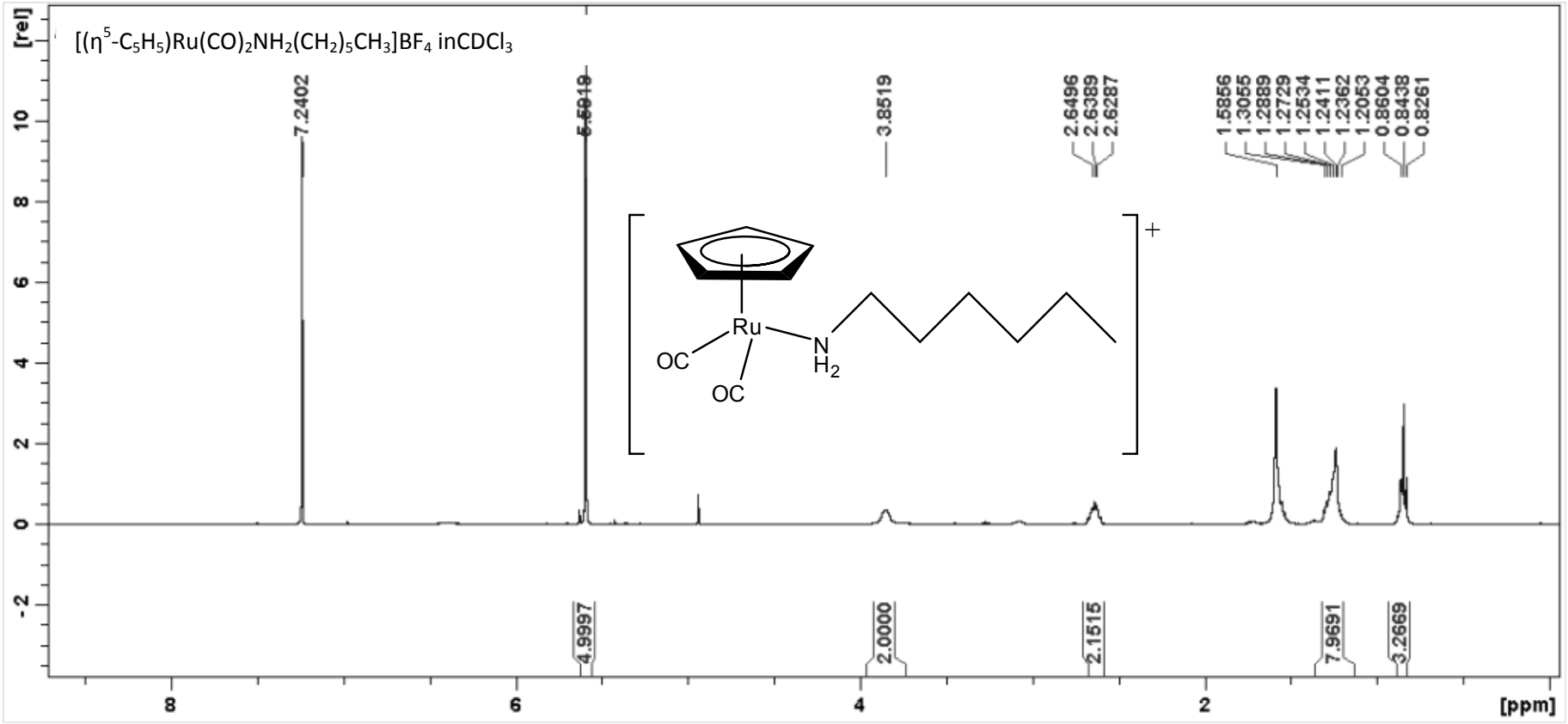

[(η5-C5H5)Ru(CO)2NH2(CH2)4CH3]BF4 in CDCl3
7.2597
5.6040
3.8860
2.6636
2.6581
2.6513
2.6440
2.6393
1.6043
1.5922
1.5800
1.2874
1.2753
1.2704
1.2655
1.2592
0.8803
0.8691
0.8576
-0.0042
Ru
OC
OC
N
H2
+
5.0010
1.9623
1.6233
2.0915
4.1039
2.7908
[rel]
[ppm]

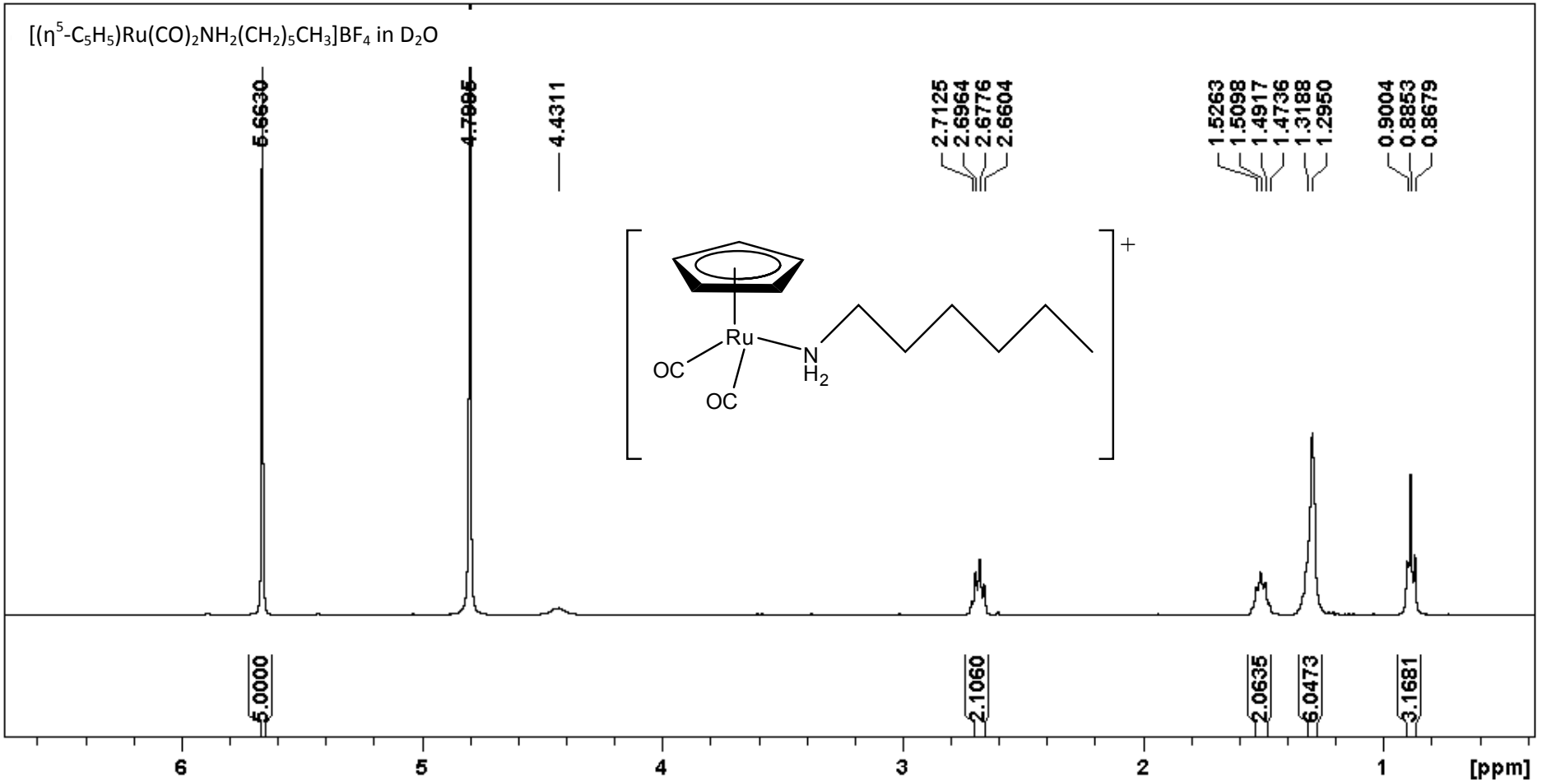

[(η5-C5H5)Ru(CO)2NH2(CH2)4CH3]BF4 in D2O
5.6636
4.7995
4.4359
2.7109
2.6926
2.6765
2.6574
1.5527
1.5340
1.5160
1.4979
1.4802
1.3417
1.3259
1.3094
1.3027
1.2946
1.2849
1.2774
1.2656
0.9063
0.8896
0.8720
Ru
OC
OC
N
H2
+
5.0000
2.0273
2.3463
2.0829
4.0284
3.3981
6
5
4
3
2
1
[ppm]

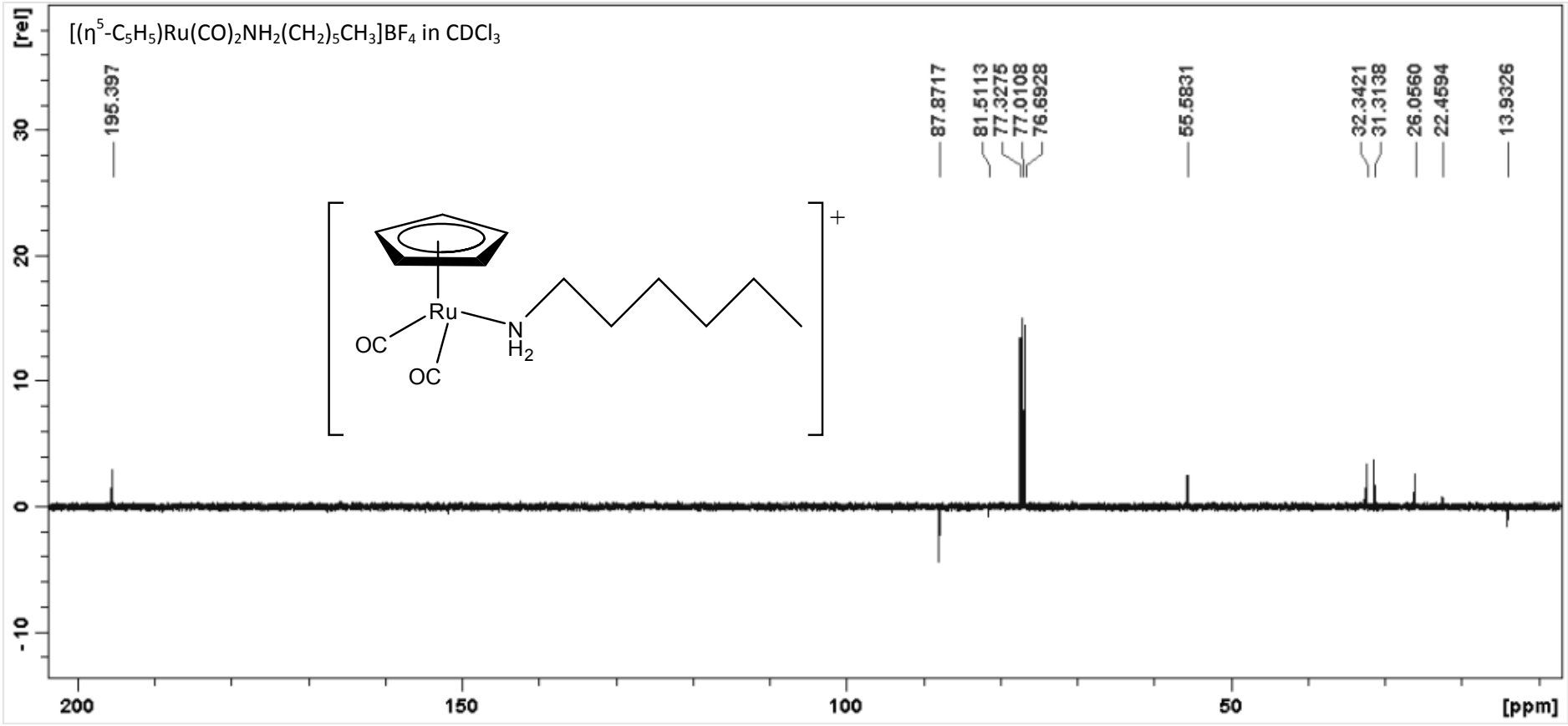

[(η5-C5H5)Ru(CO)2NH2(CH2)4CH3]BF4 in CDCl3
[rel]
20
0
-20
195.4362
87.8560
77.2273
77.0157
76.8039
55.5086
32.0439
28.4346
22.2143
13.8506
Ru
OC
OC
N
H2
+
200
150
100
50
0
[ppm]

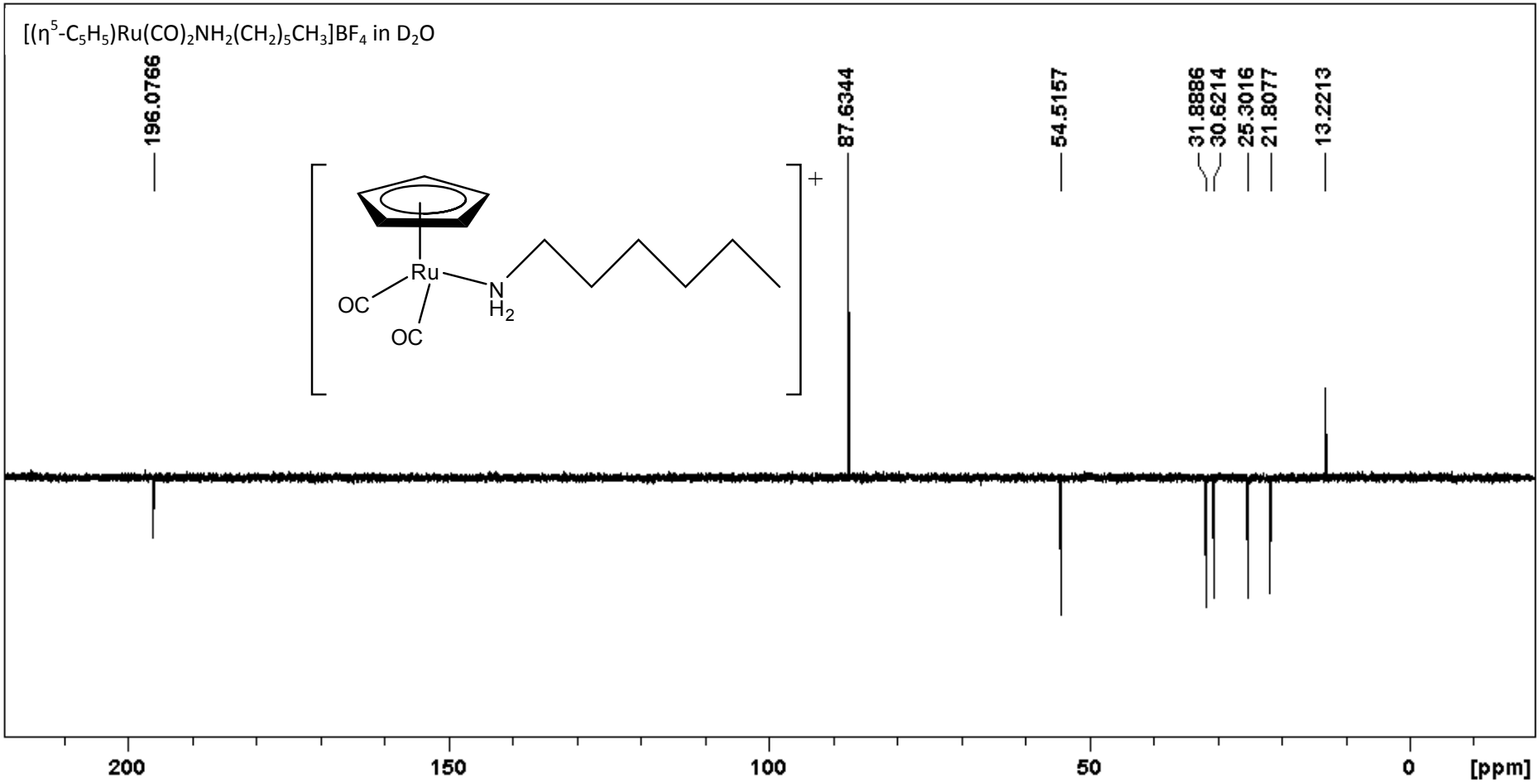

[(η5-C5H5)Ru(CO)2NH2(CH2)4CH3]BF4 in D2O
196.0803
87.6327
54.6323
54.4995
31.6315
27.8245
21.5888
13.1130
Ru
OC
OC
N
H2
+
200
150
100
50
0
[ppm]

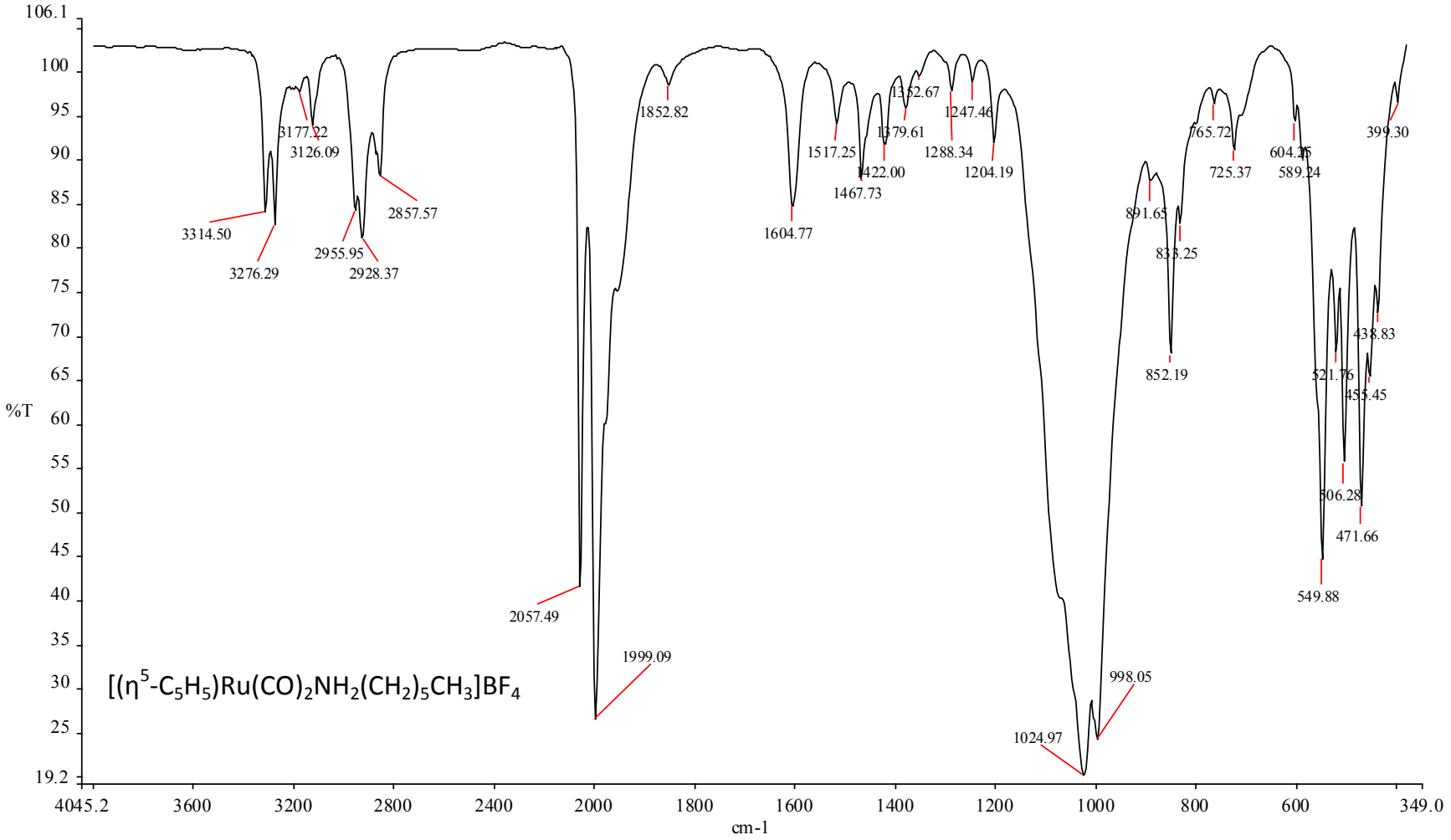

94.0
90
85
80
75
70
65
60
55
50
45
41.3
%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
380.0
cm-1
3935.76
3321.05
3279.89
3173.36
3126.16
2942.29
2865.54
2052.51
1997.44
1598.90
1465.47
1427.24
1417.94
1379.65
1363.75
1290.27
1266.54
1204.99
1181.62
1030.10
997.16
892.28
854.66
833.94
767.12
728.24
697.17
603.23
547.89
521.98
504.06
464.43
391.46
Ru
OC
OC
N
H2
+

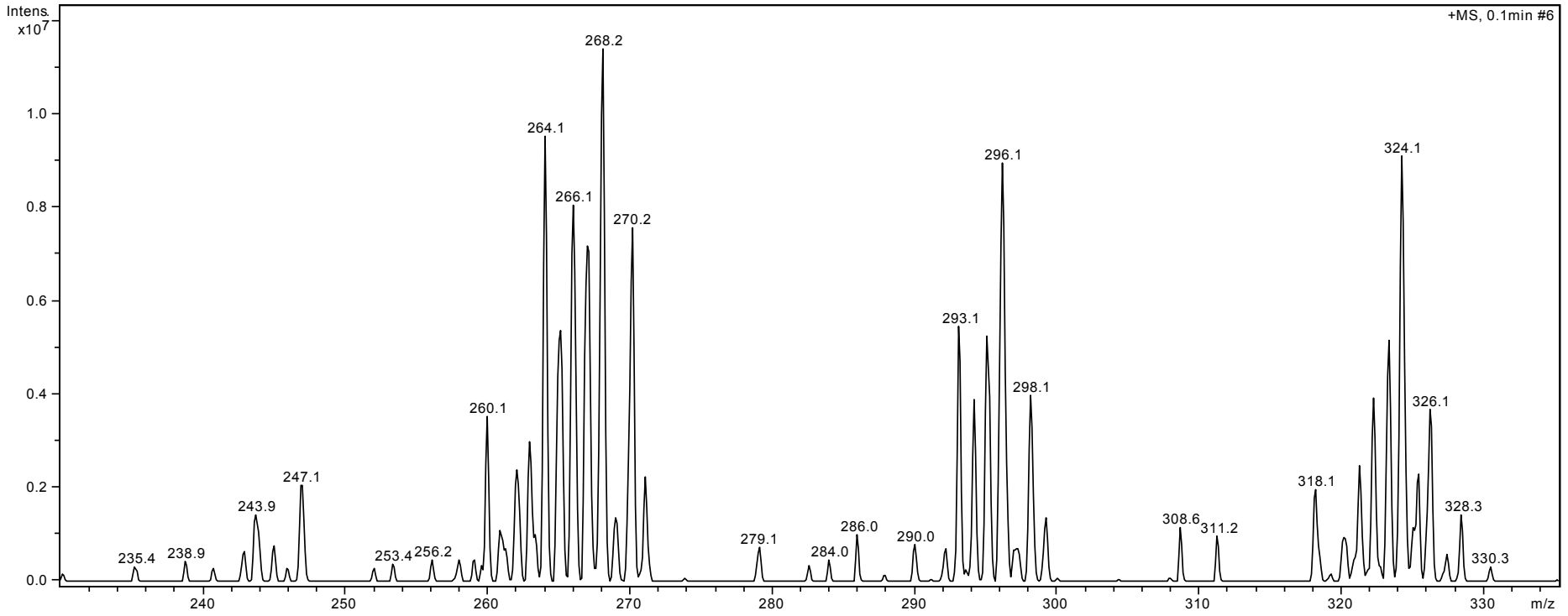

[(η5-C5H5)Ru(CO)2NH2(CH2)5CH3]BF4 inCDCl3
[rel]
7.2402
5.5819
3.8519
2.6496
2.6389
2.6287
1.5856
1.3055
1.2889
1.2729
1.2534
1.2411
1.2362
1.2053
0.8604
0.8438
0.8261
Ru
OC
OC
N
H2
+
4.9997
2.0000
2.1515
7.9691
3.2669
[ppm]


[(η5-C5H5)Ru(CO)2NH2(CH2)5CH3]BF4 in D2O
5.6630
4.7995
4.4311
2.7125
2.6964
2.6776
2.6604
1.5263
1.5098
1.4917
1.4736
1.3188
1.2950
0.9004
0.8853
0.8679
Ru
OC
OC
N
H2
+
5.0000
2.1060
2.0635
6.0473
3.1681
6
5
4
3
2
1
[ppm]

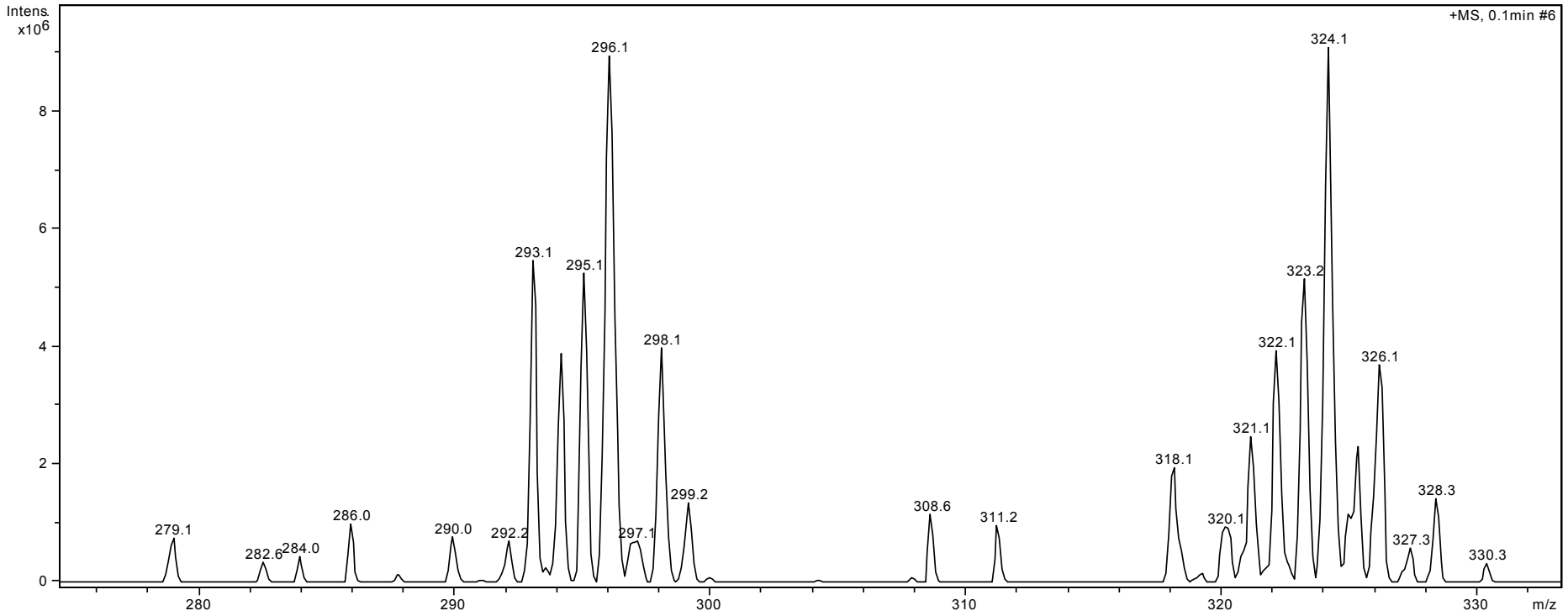

[(η5-C5H5)Ru(CO)2NH2(CH2)5CH3]BF4 in CDCl3
195.397
87.8717
81.5113
77.3275
77.0108
76.6928
55.5831
32.3421
31.3138
26.0560
22.4594
13.9326
Ru
OC
OC
N
H2
+
[rel]
30
20
10
0
-10
200
150
100
50
[ppm]


[(η5-C5H5)Ru(CO)2NH2(CH2)5CH3]BF4 in D2O
196.0766
87.6344
54.5157
31.8886
30.6214
25.3016
21.8077
13.2213
Ru
OC
OC
N
H2
+
200
150
100
50
0
[ppm]


106.1
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
19.2
%T
4045.2
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
349.0
cm-1
3314.50
3276.29
3177.22
3126.09
2955.95
2928.37
2857.57
2057.49
1999.09
1852.82
1604.77
1517.25
1467.73
1422.00
1379.61
1352.67
1288.34
1247.46
1204.19
1024.97
998.05
891.65
852.19
833.25
765.72
725.37
604.45
589.24
549.88
521.76
506.28
471.66
455.45
438.83
399.30
[(η5-C5H5)Ru(CO)2NH2(CH2)5CH3]BF4

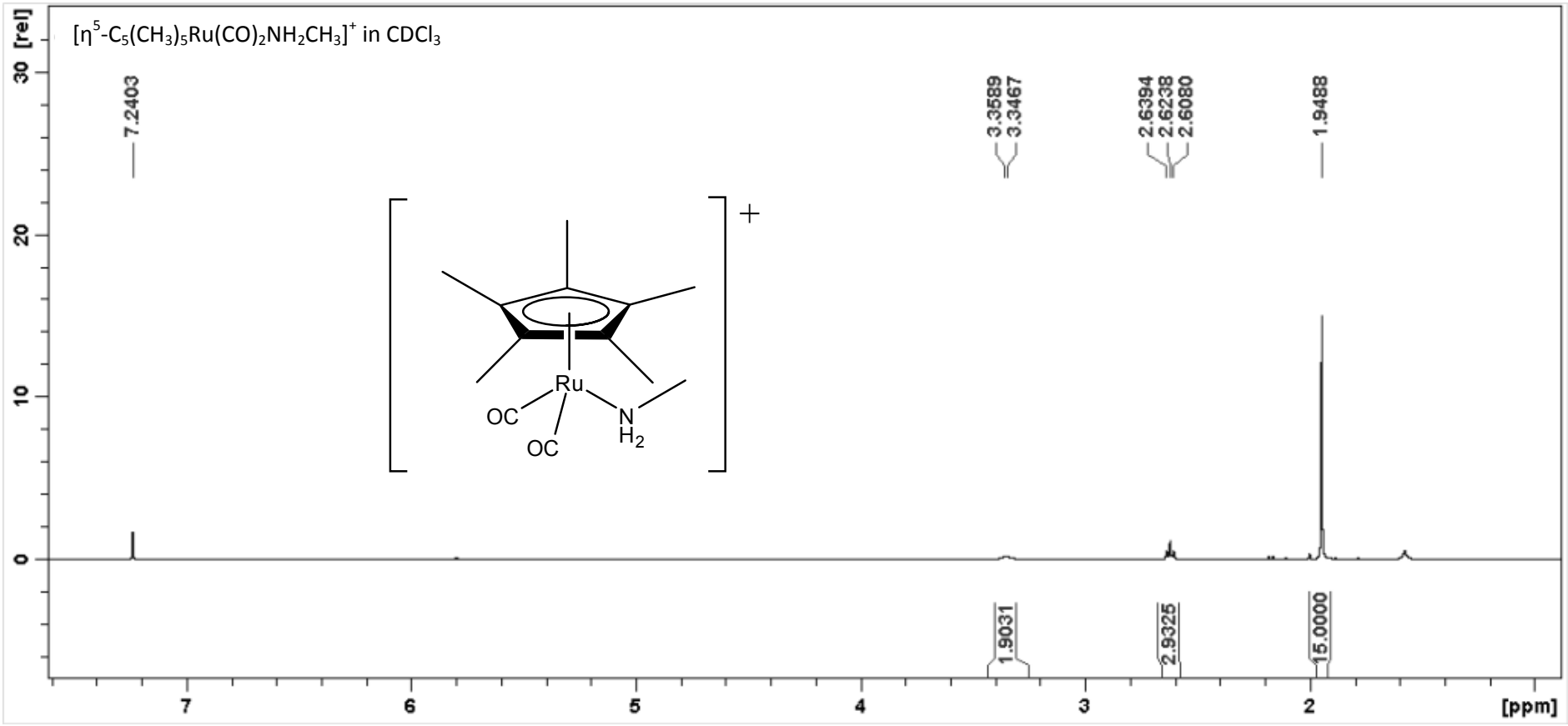


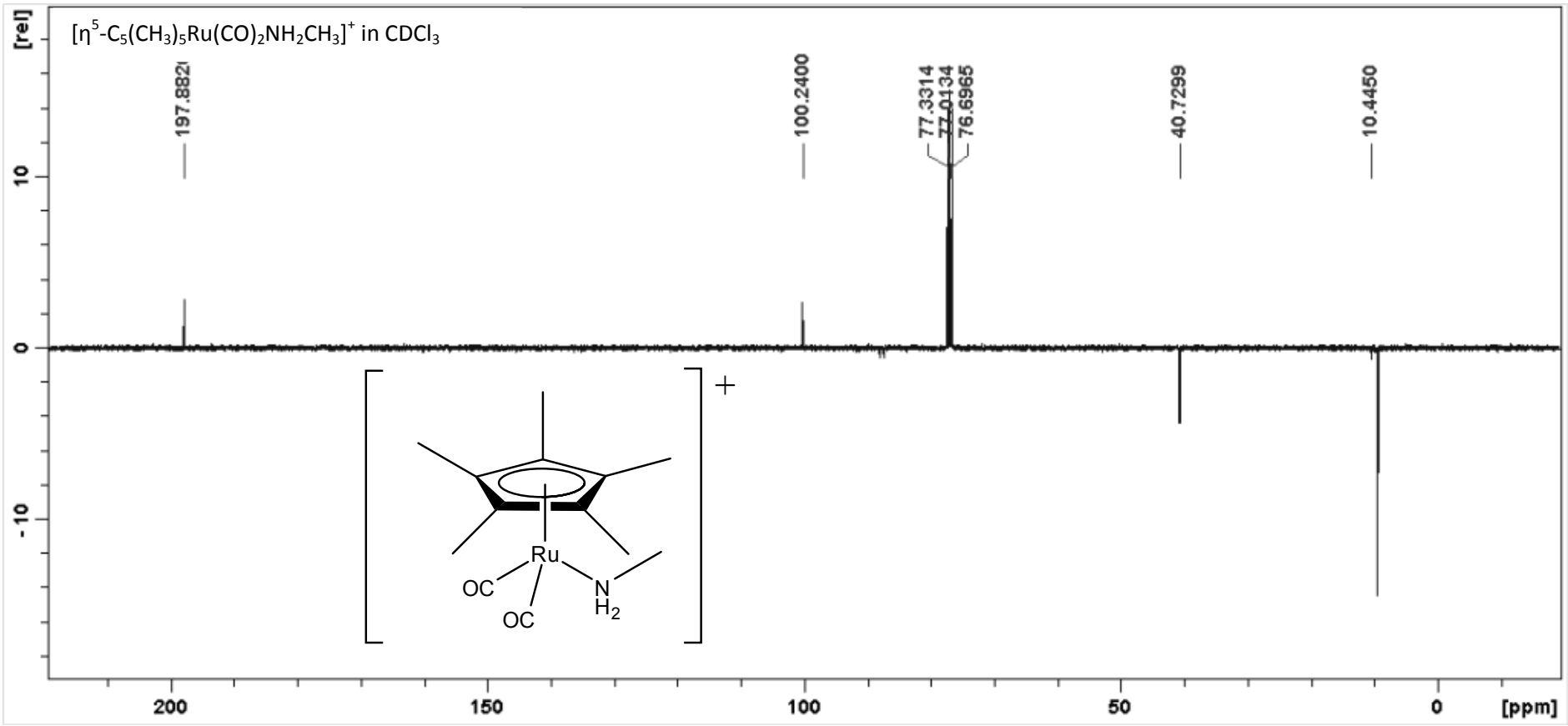

$[(\eta^5\text{-}C_5H_5)Ru(CO)_2NH_2(CH_2)_5CH_3]$ $[(\eta^5\text{-}C_5H_5)Ru(CO)NH_2(CH_2)_5CH_3]$ $[(\eta^5\text{-}C_5H_5)Ru(CO)_2NH_2(CH_2)_5CH_3]$

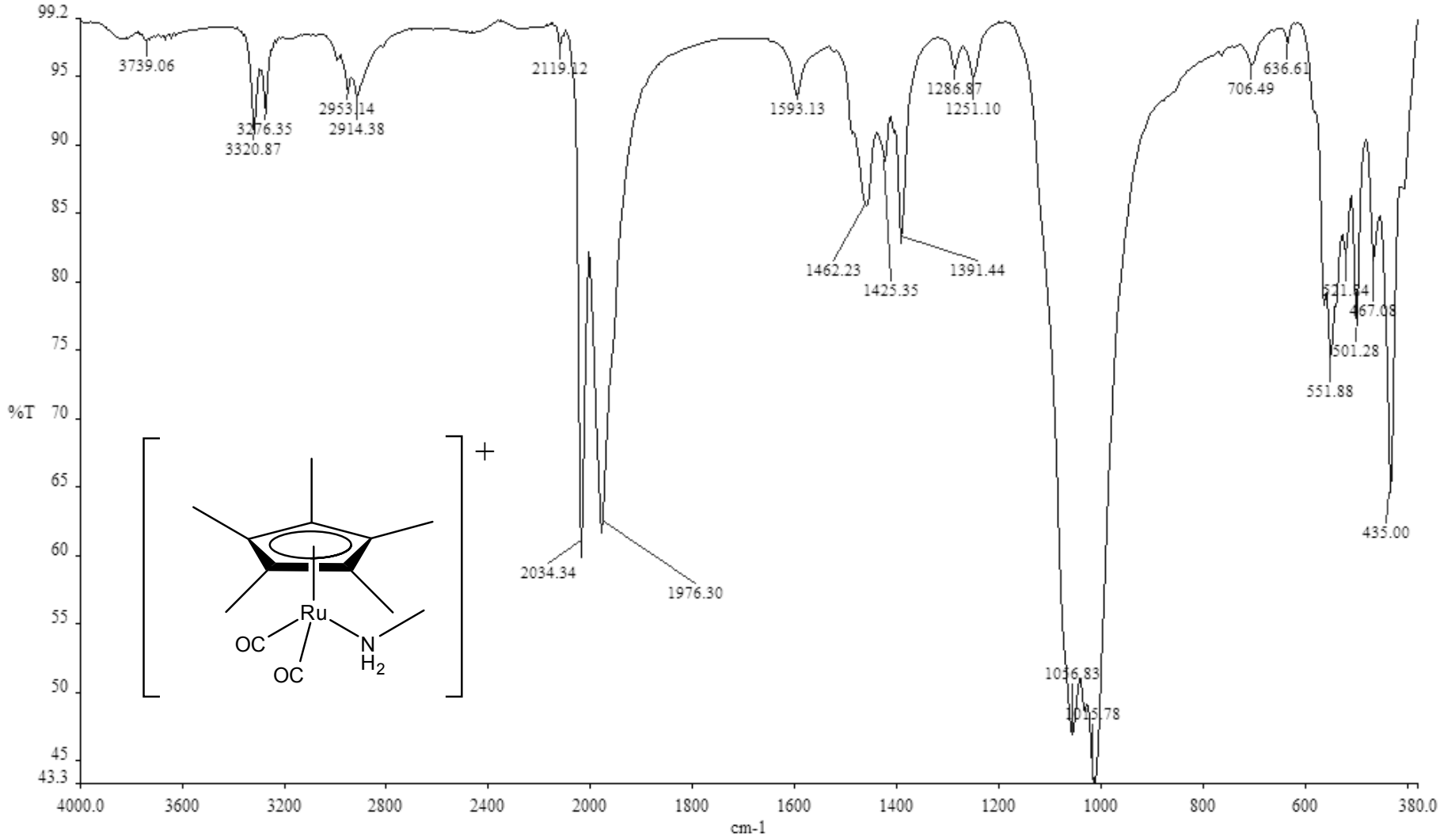


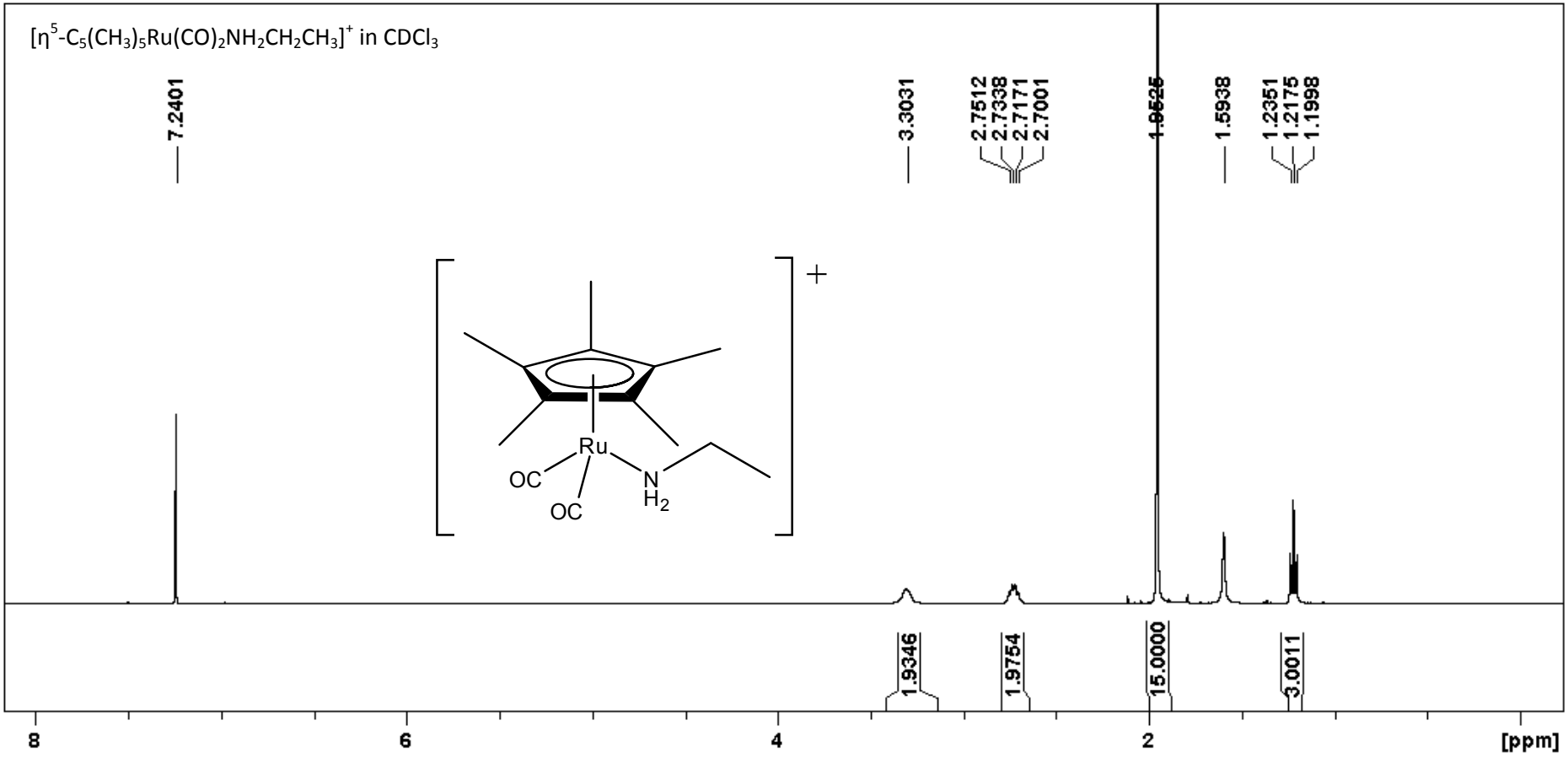

$[(\eta^5\text{-}C_5H_5)Ru(CO)NH_2(CH_2)_5CH_3]$ $[(\eta^5\text{-}C_5H_5)Ru(CO)_2NH_2(CH_2)_5CH_3]$

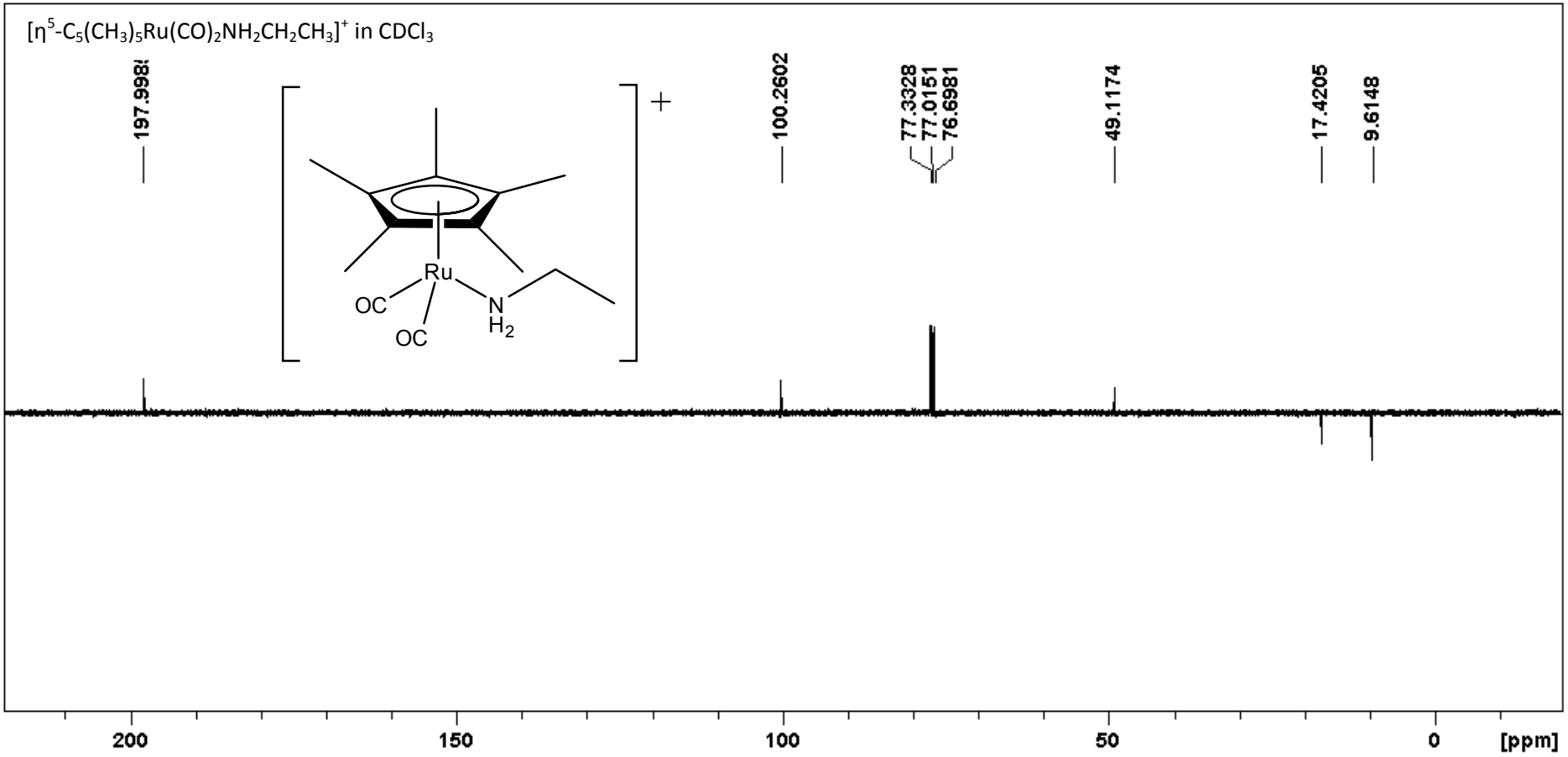
**SPECTRAL DATA PERTAINING TO CHAPTER 4**

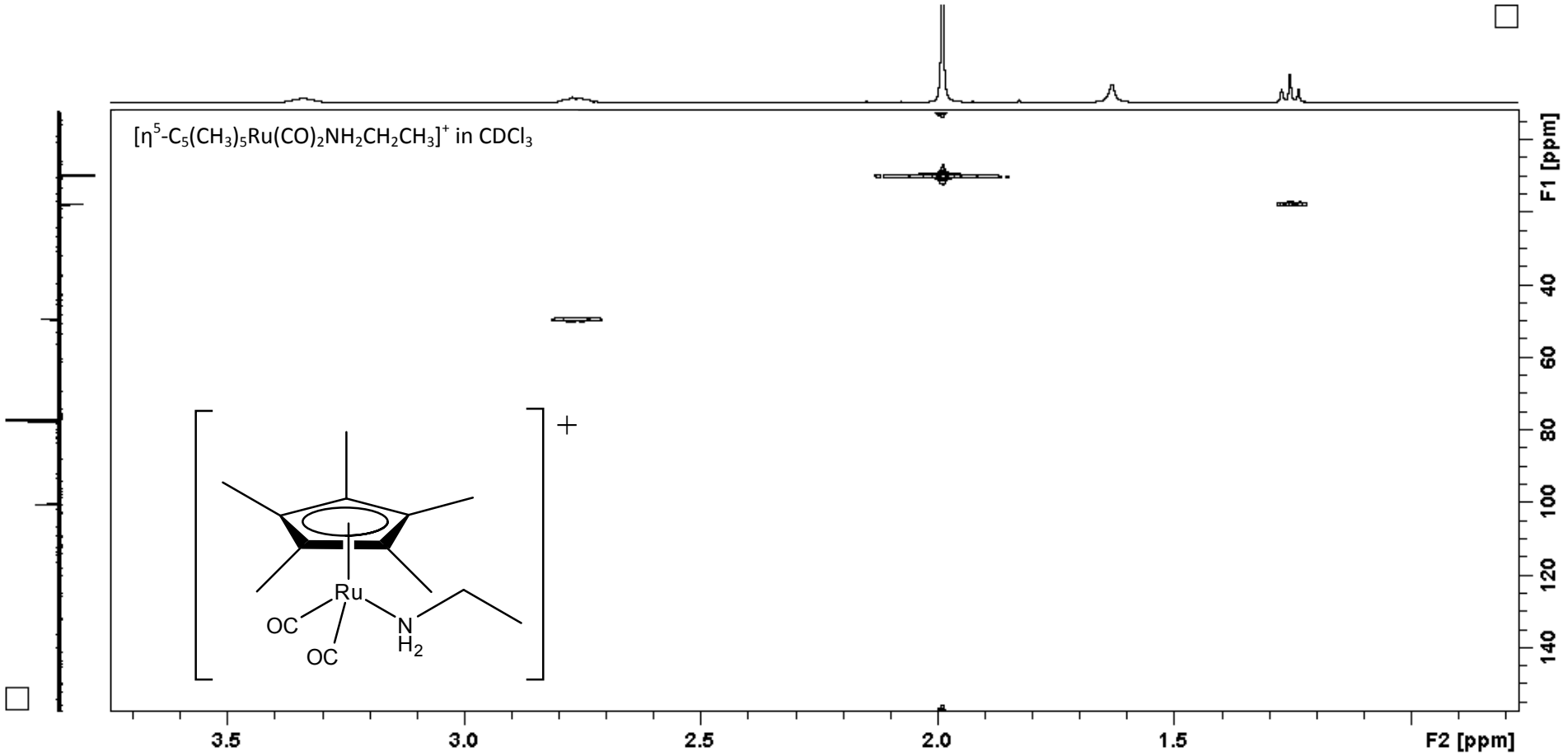


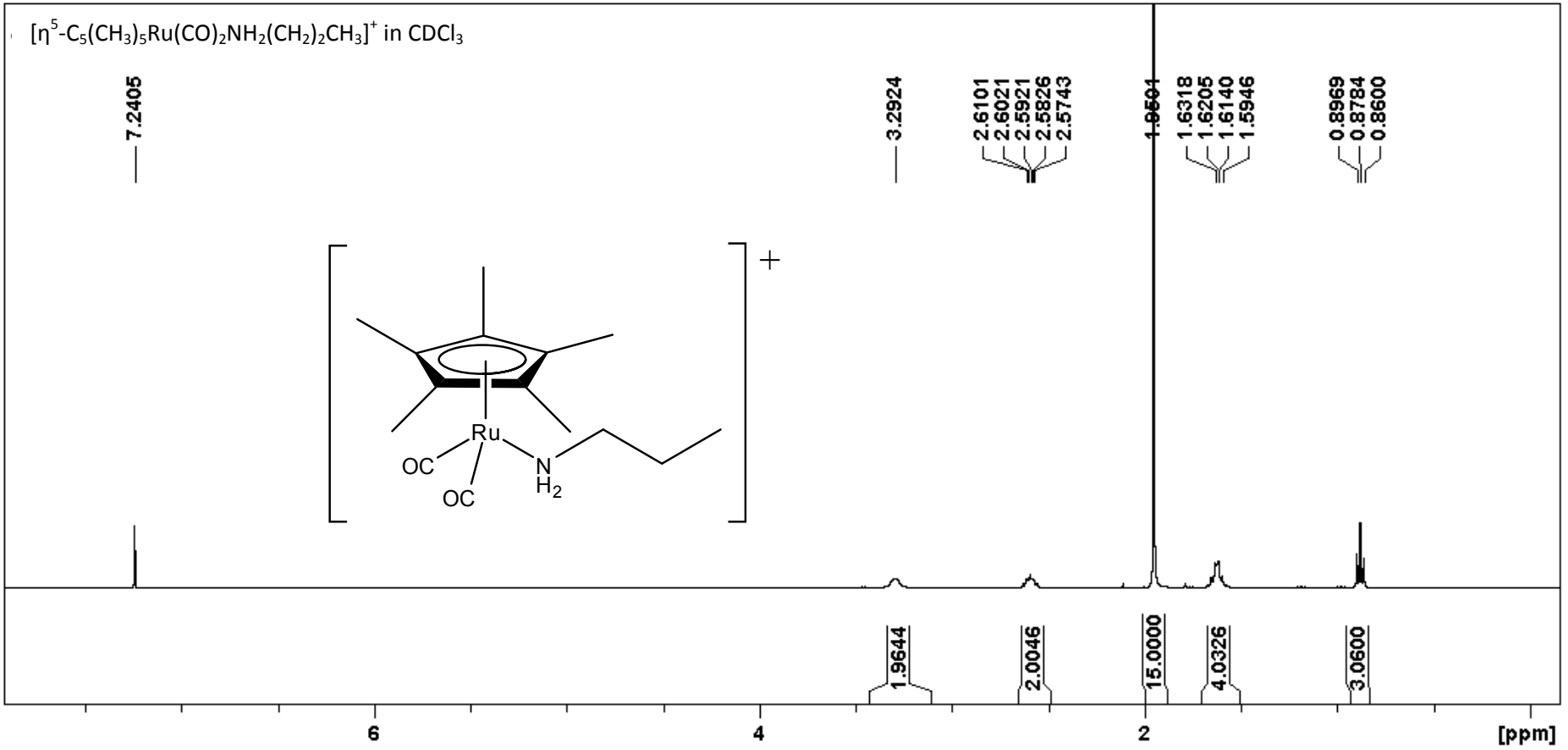

[η5-C5(CH3)5Ru(CO)2NH2CH3]+ in CDCl3
[rel]
10
0
-10
197.8821
100.2400
77.3314
77.0134
76.6965
40.7299
10.4450
Ru
OC
OC
N
H2
+
200
150
100
50
0
[ppm]

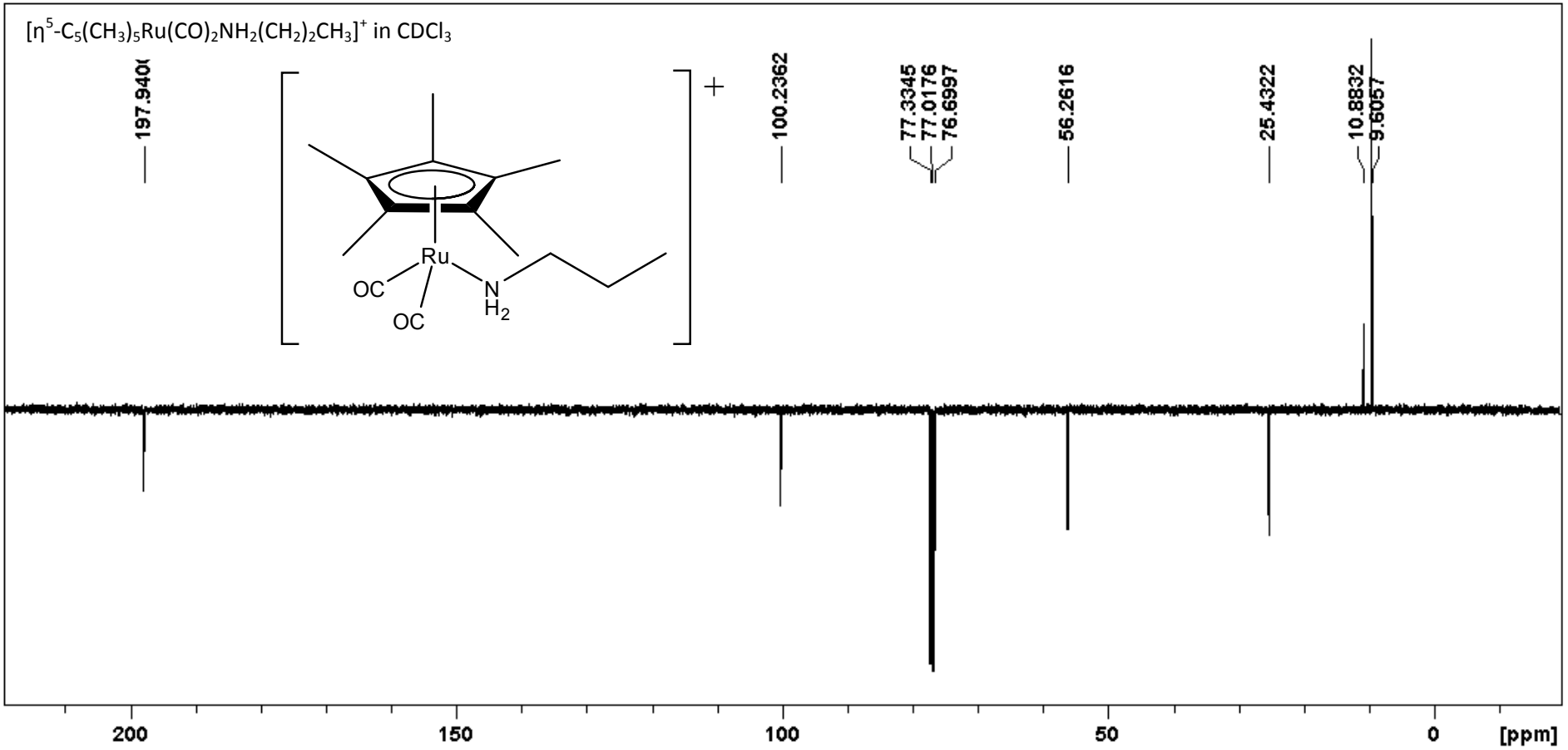

99.2
95
90
85
80
75
%T 70
65
60
55
50
45
43.3
3739.06
3320.87
3276.35
2953.14
2914.38
2119.12
2034.34
1976.30
1593.13
1462.23
1425.35
1391.44
1286.87
1251.10
1056.83
1015.78
706.49
636.61
551.88
501.28
467.08
435.00
Ru
OC
OC
N
H2
+
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
380.0
cm-1

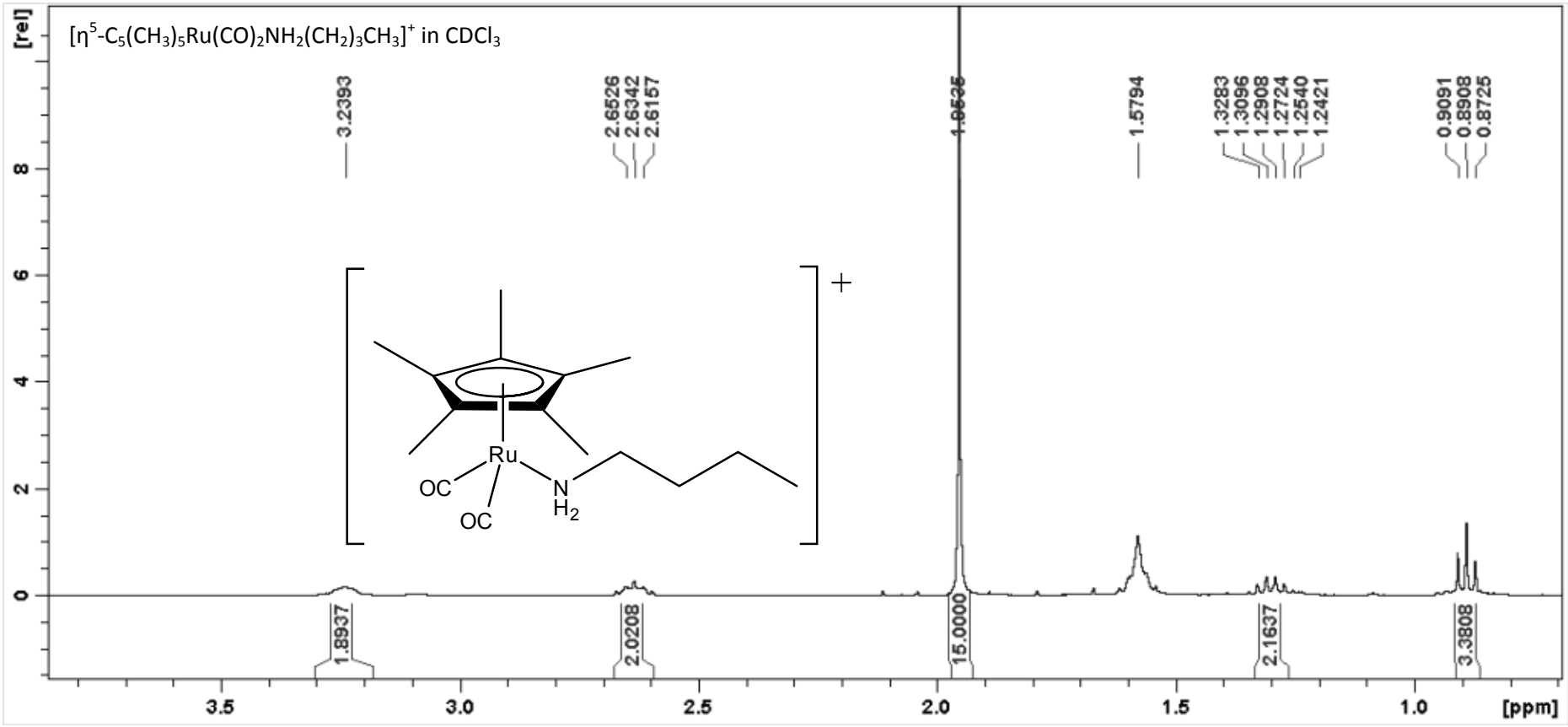

[η5-C5(CH3)5Ru(CO)2NH2CH2CH3]+ in CDCl3
7.2401
3.3031
2.7512
2.7338
2.7171
2.7001
1.9525
1.5938
1.2351
1.2175
1.1998
Ru
OC
OC
N
H2
+
1.9346
1.9754
15.0000
3.0011
8
6
4
2
[ppm]

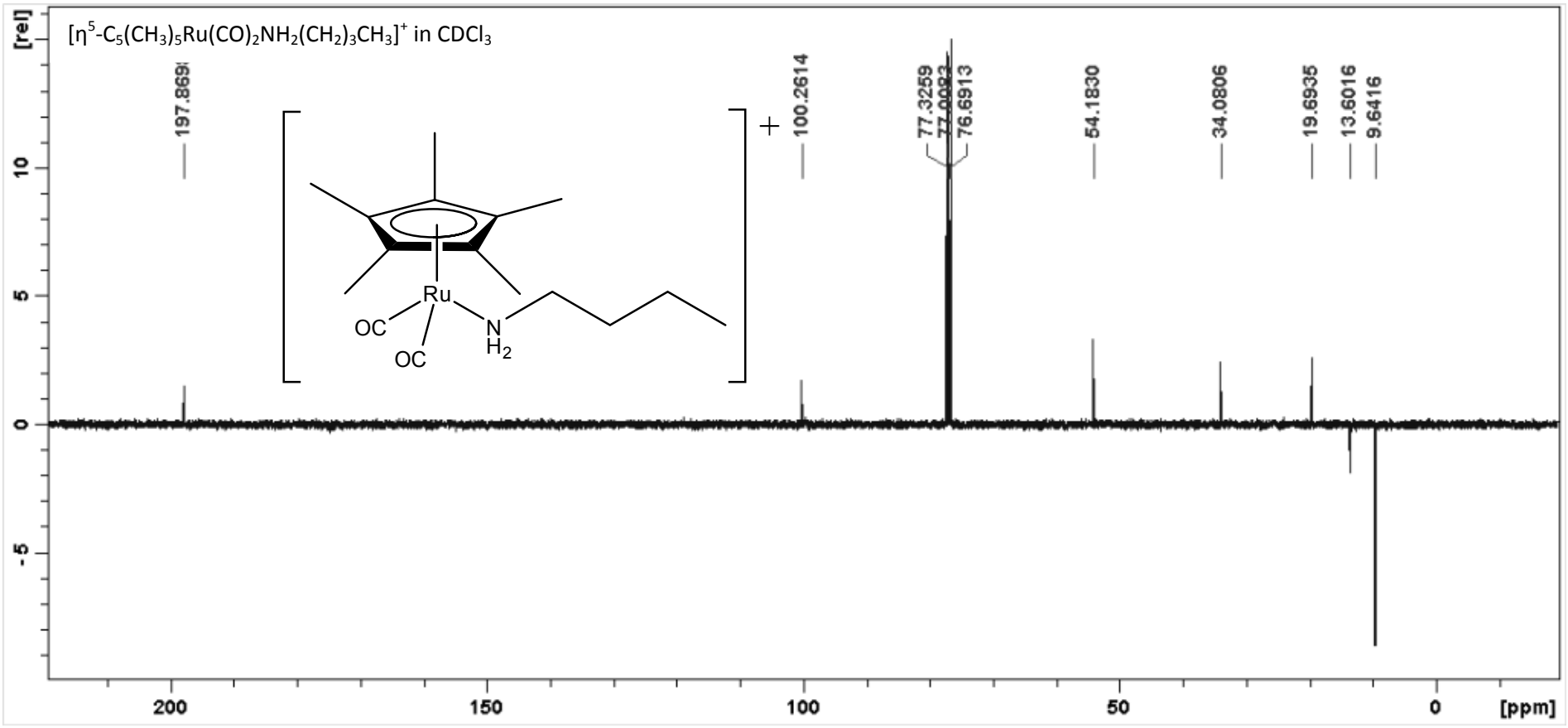

[η5-C5(CH3)5Ru(CO)2NH2CH2CH3]+ in CDCl3
197.998
100.2602
77.3328
77.0151
76.6981
49.1174
17.4205
9.6148
Ru
OC
OC
N
H2
200
150
100
50
0
[ppm]

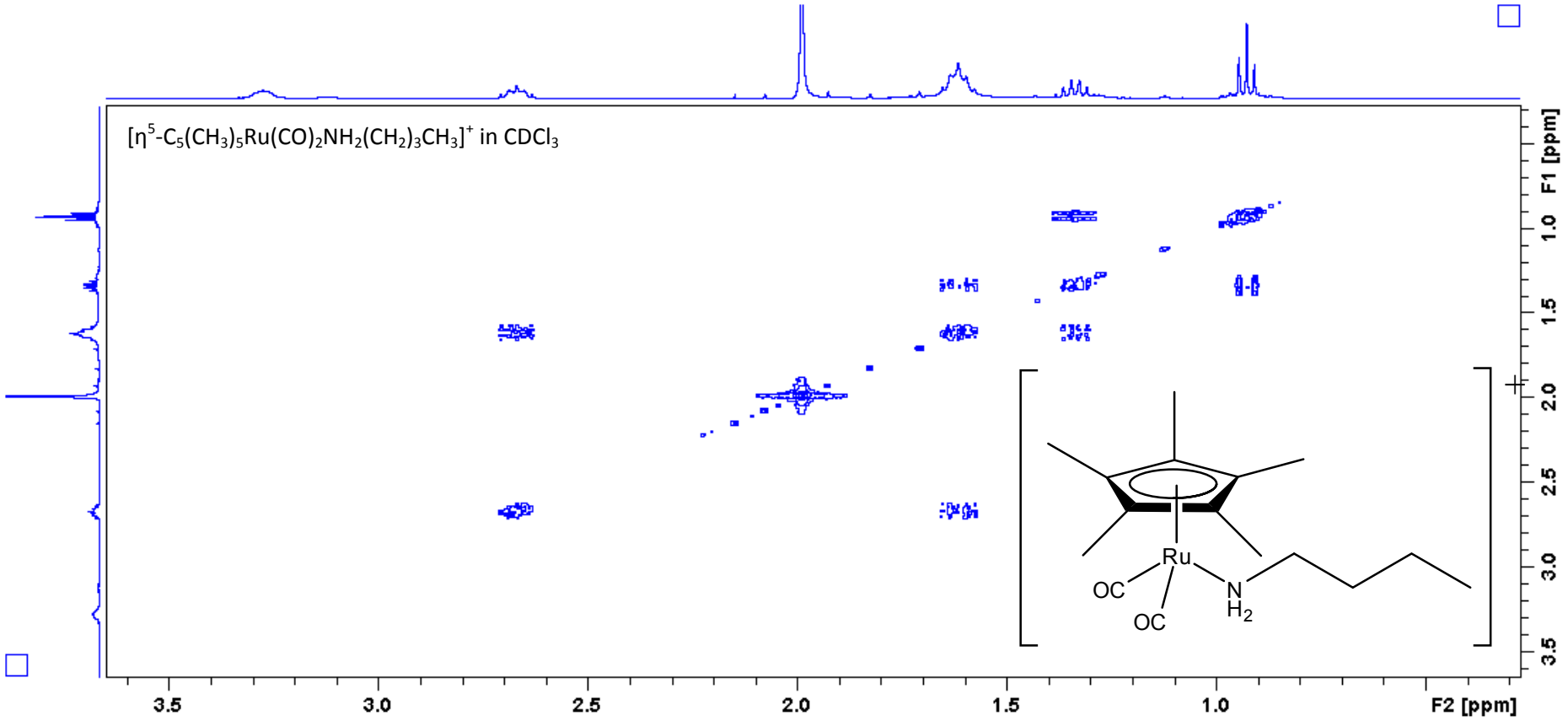

[η5-C5(CH3)5Ru(CO)2NH2CH2CH3]+ in CDCl3
Ru
OC
OC
N
H2
+
F1 [ppm]
40
60
80
100
120
140
3.5
3.0
2.5
2.0
1.5
F2 [ppm]

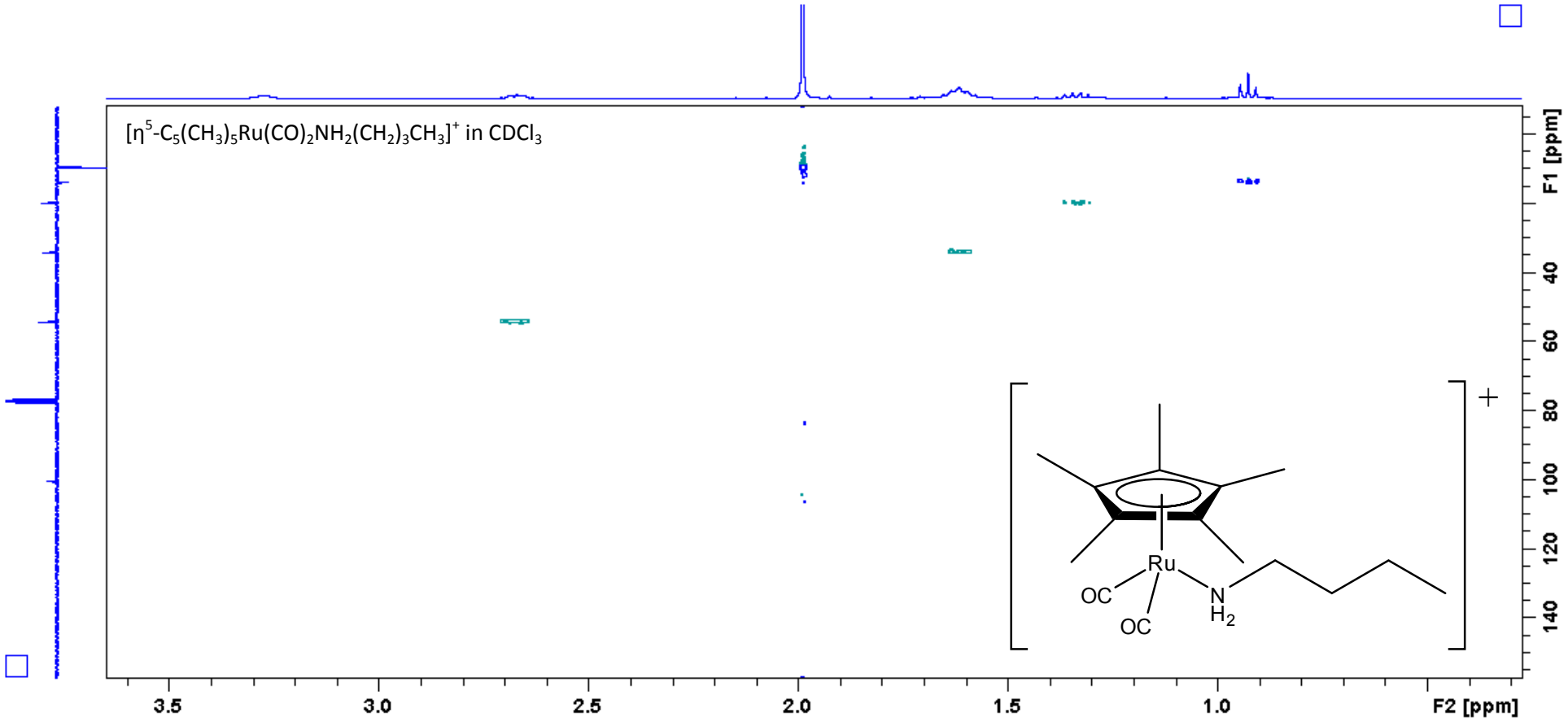

[η5-C5(CH3)5Ru(CO)2NH2(CH2)2CH3]+ in CDCl3
7.2405
3.2924
2.6101
2.6021
2.5921
2.5826
2.5743
1.9501
1.6318
1.6205
1.6140
1.5946
0.8969
0.8784
0.8600
Ru
OC
OC
N
H2
+
1.9644
2.0046
15.0000
4.0326
3.0600
6
4
2
[ppm]

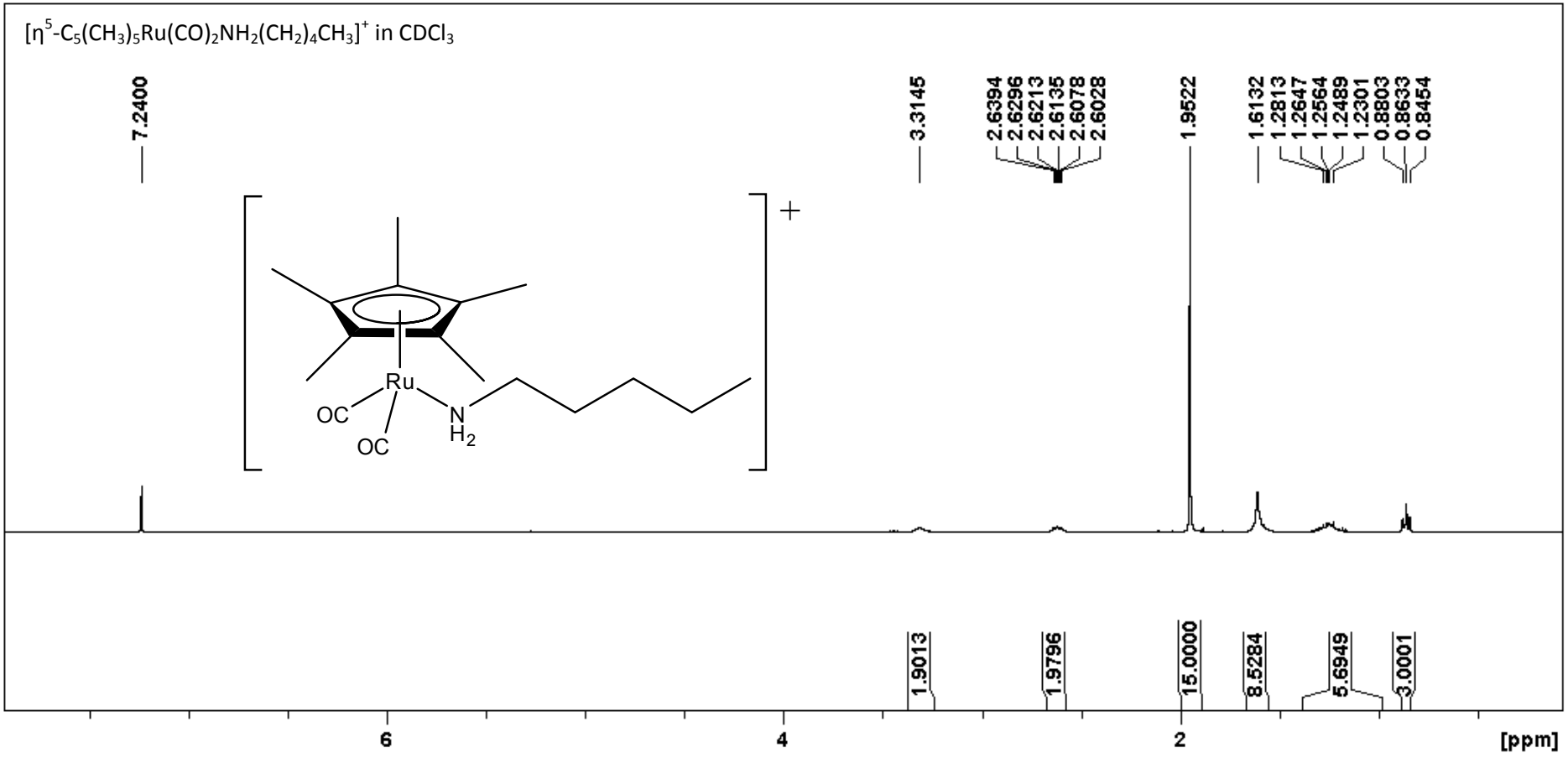

[η5-C5(CH3)5Ru(CO)2NH2(CH2)2CH3]+ in CDCl3
197.940
100.2362
77.3345
77.0176
76.6997
56.2616
25.4322
10.8832
9.6057
Ru
OC
OC
N
H2
200
150
100
50
0
[ppm]

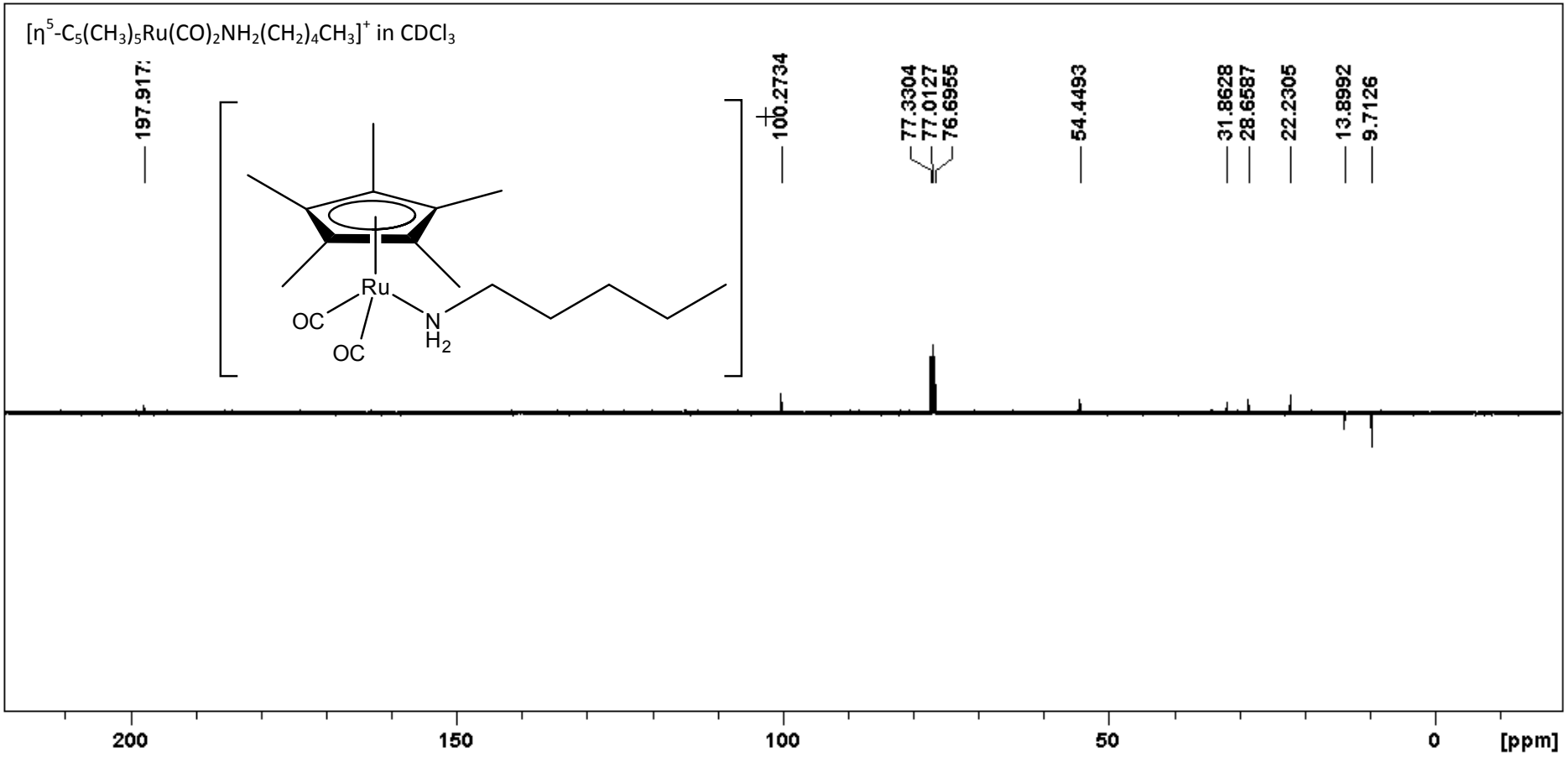

[η5-C5(CH3)5Ru(CO)2NH2(CH2)3CH3]+ in CDCl3
[rel]
3.2393
2.6526
2.6342
2.6157
1.5794
1.3283
1.3096
1.2908
1.2724
1.2540
1.2421
0.9091
0.8908
0.8725
Ru
OC
OC
N
H2
+
1.8937
2.0208
15.0000
2.1637
3.3808
3.5
3.0
2.5
2.0
1.5
1.0
[ppm]


[η5-C5(CH3)5Ru(CO)2NH2(CH2)3CH3]+ in CDCl3
[rel]
197.869
100.2614
77.3259
77.0083
76.6913
54.1830
34.0806
19.6935
13.6016
9.6416
Ru
OC
OC
N
H2
10
5
0
-5
200
150
100
50
0
[ppm]

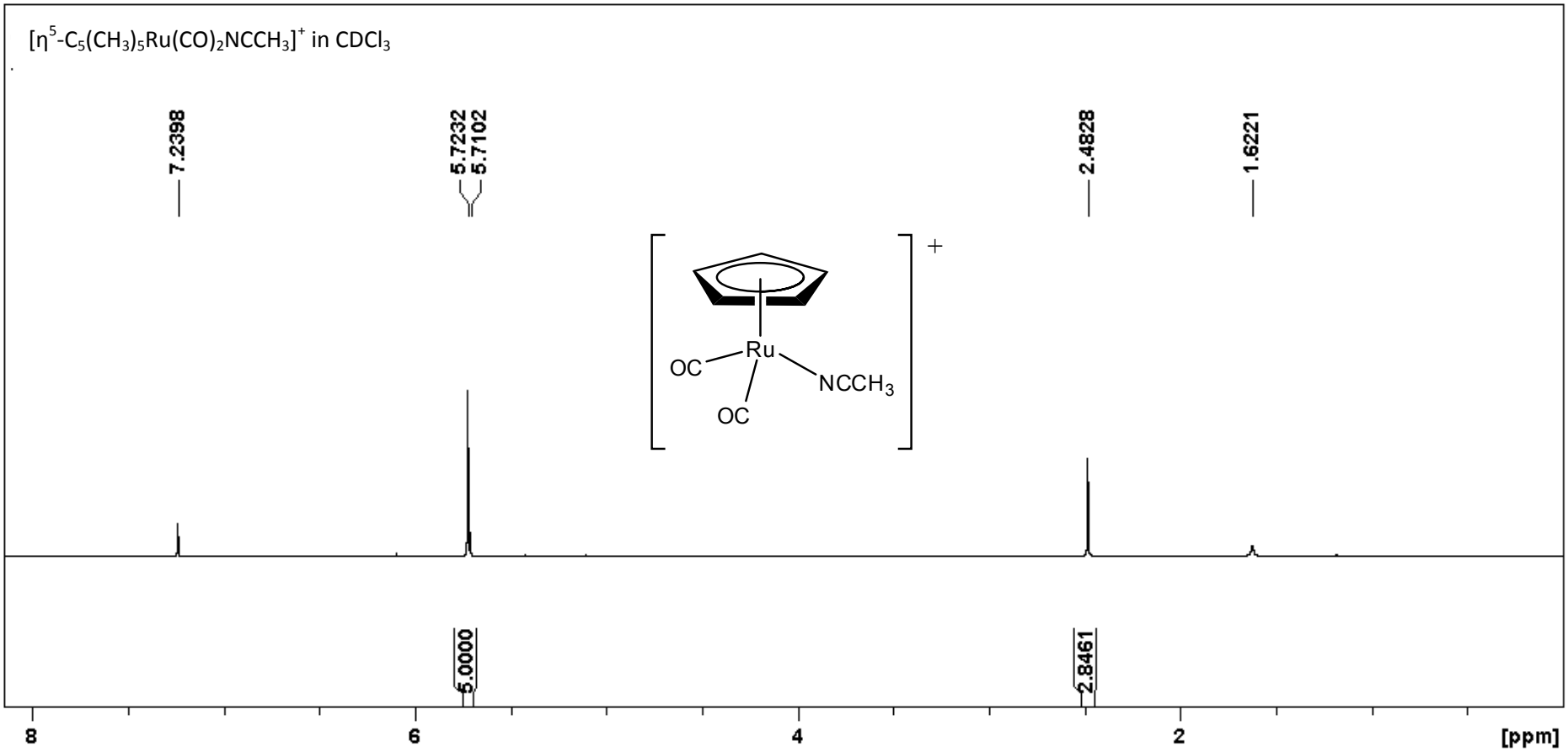

[η5-C5(CH3)5Ru(CO)2NH2(CH2)3CH3]+ in CDCl3
F1 [ppm]
F2 [ppm]
3.5
3.0
2.5
2.0
1.5
1.0
Ru
OC
OC
N
H2

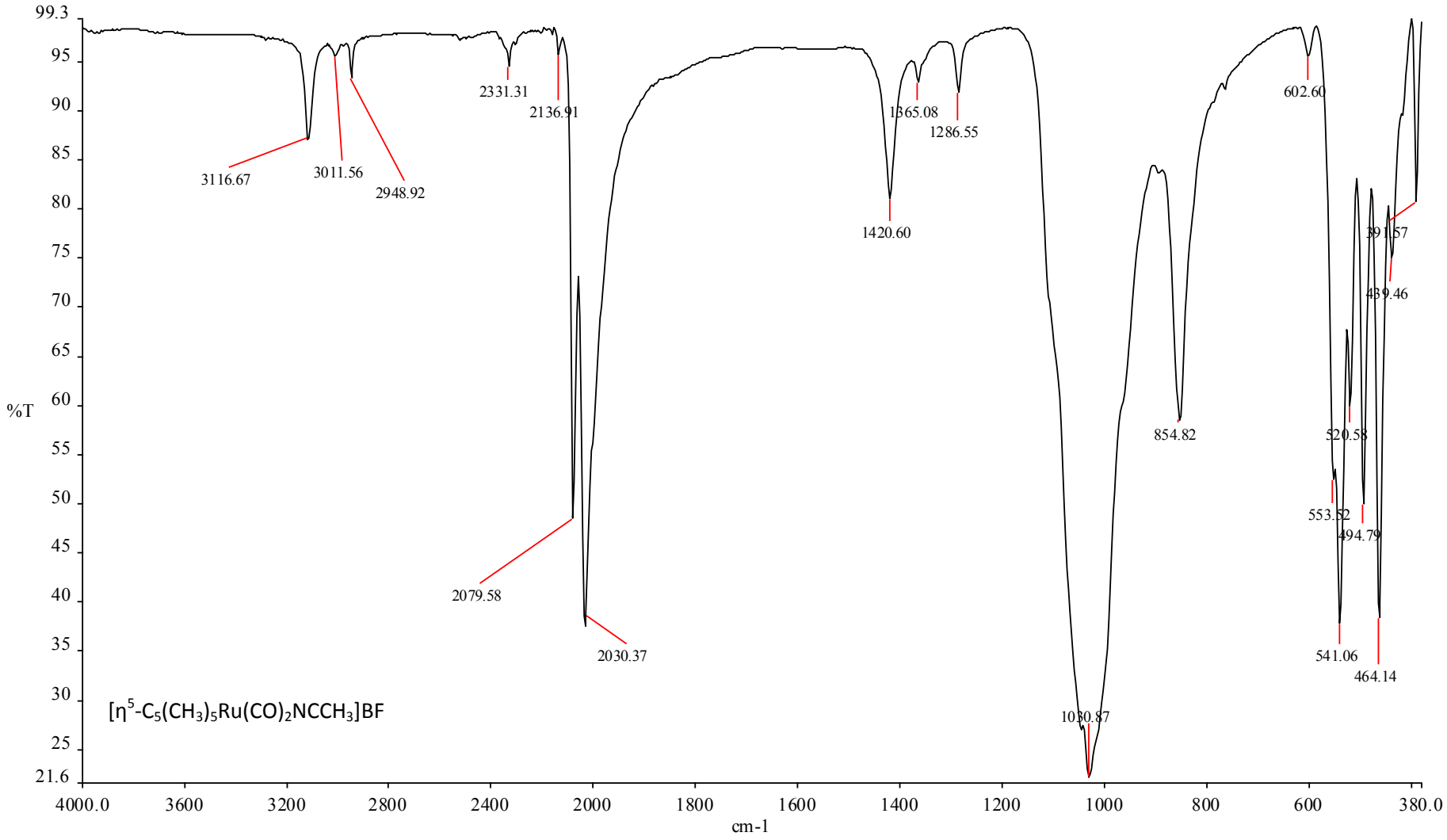

[η5-C5(CH3)5Ru(CO)2NH2(CH2)3CH3]+ in CDCl3
F1 [ppm]
40
60
80
100
120
140
3.5
3.0
2.5
2.0
1.5
1.0
F2 [ppm]
Ru
OC
OC
N
H2
+

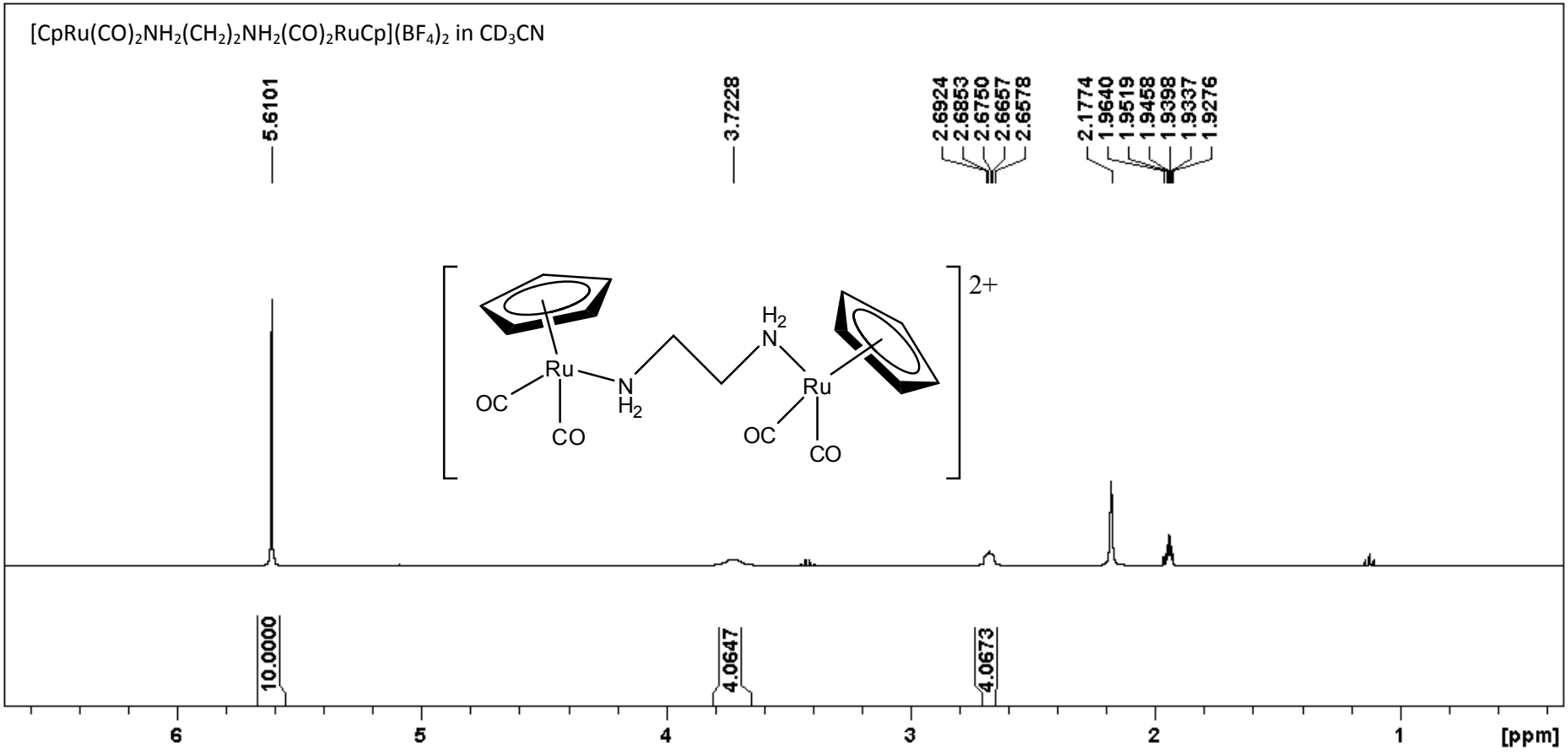

[η5-C5(CH3)5Ru(CO)2NH2(CH2)4CH3]+ in CDCl3
7.2400
3.3145
2.6394
2.6296
2.6213
2.6135
2.6078
2.6028
1.9522
1.6132
1.2813
1.2647
1.2564
1.2489
1.2301
0.8803
0.8633
0.8454
Ru
OC
OC
N
H2
+
1.9013
1.9796
15.0000
8.5284
5.6949
3.0001
6
4
2
[ppm]

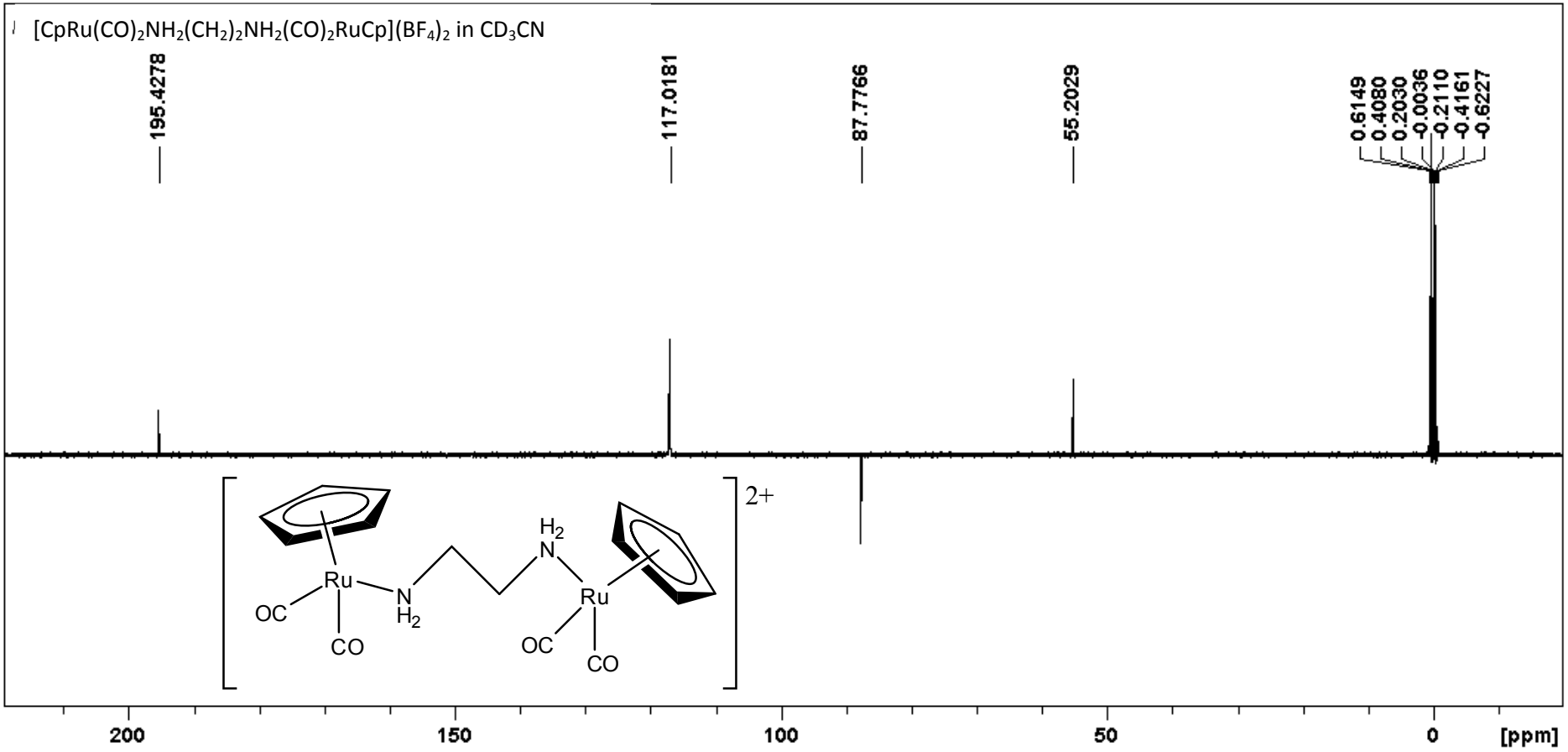

[η5-C5(CH3)5Ru(CO)2NH2(CH2)4CH3]+ in CDCl3
197.917
100.2734
77.3304
77.0127
76.6955
54.4493
31.8628
28.6587
22.2305
13.8992
9.7126
Ru
OC
OC
N
H2
200
150
100
50
0
[ppm]

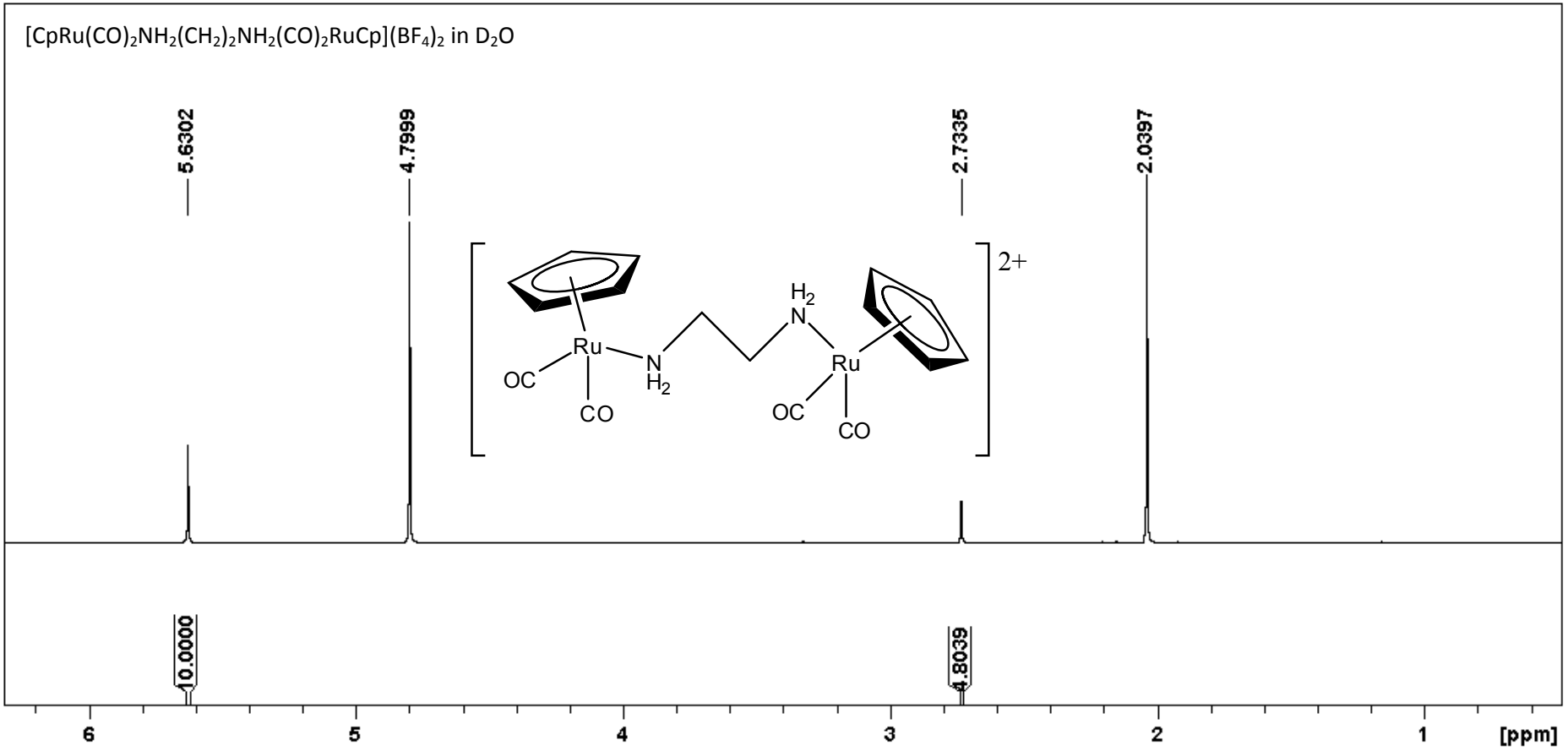
**SPECTRAL DATA PERTAINING TO CHAPTER 5**

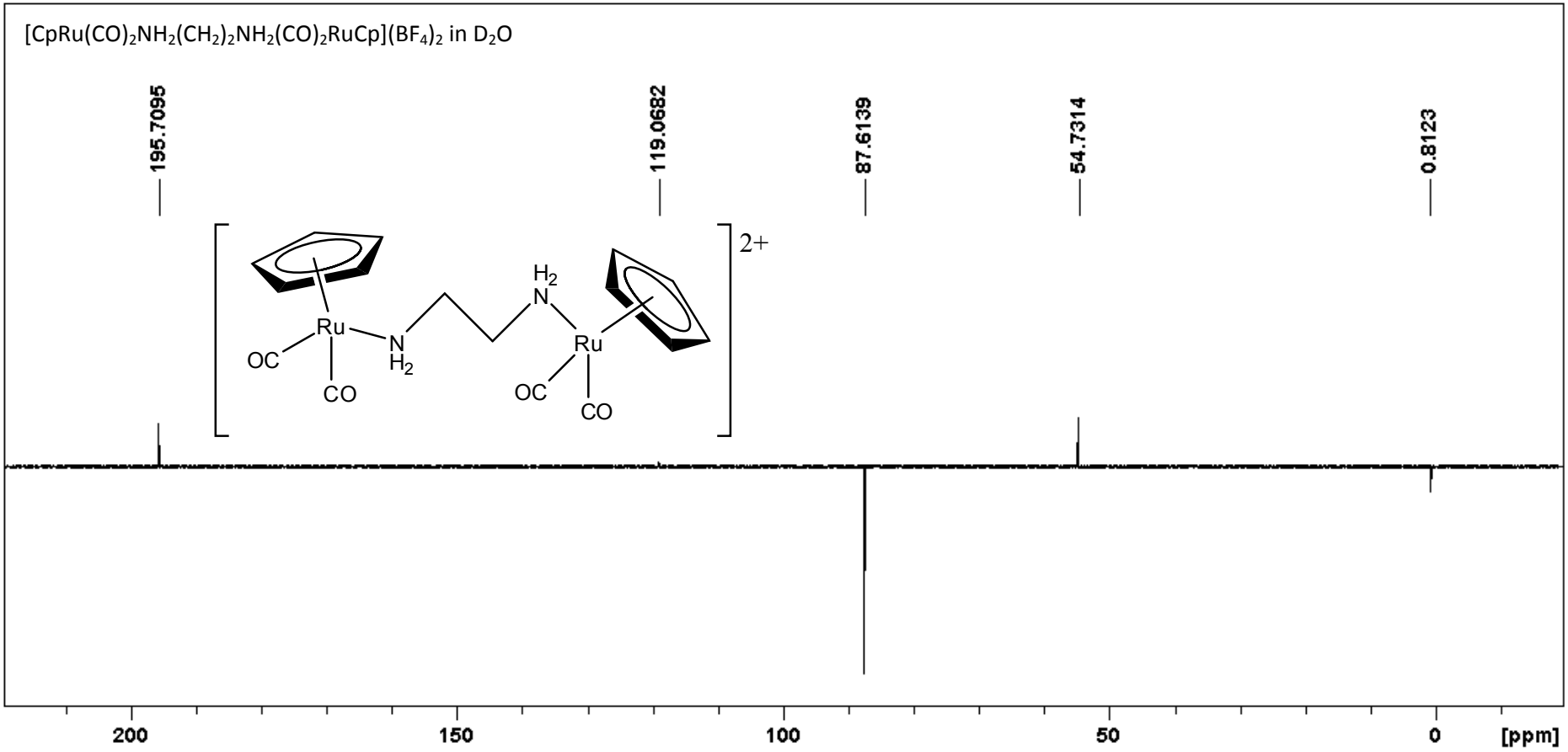


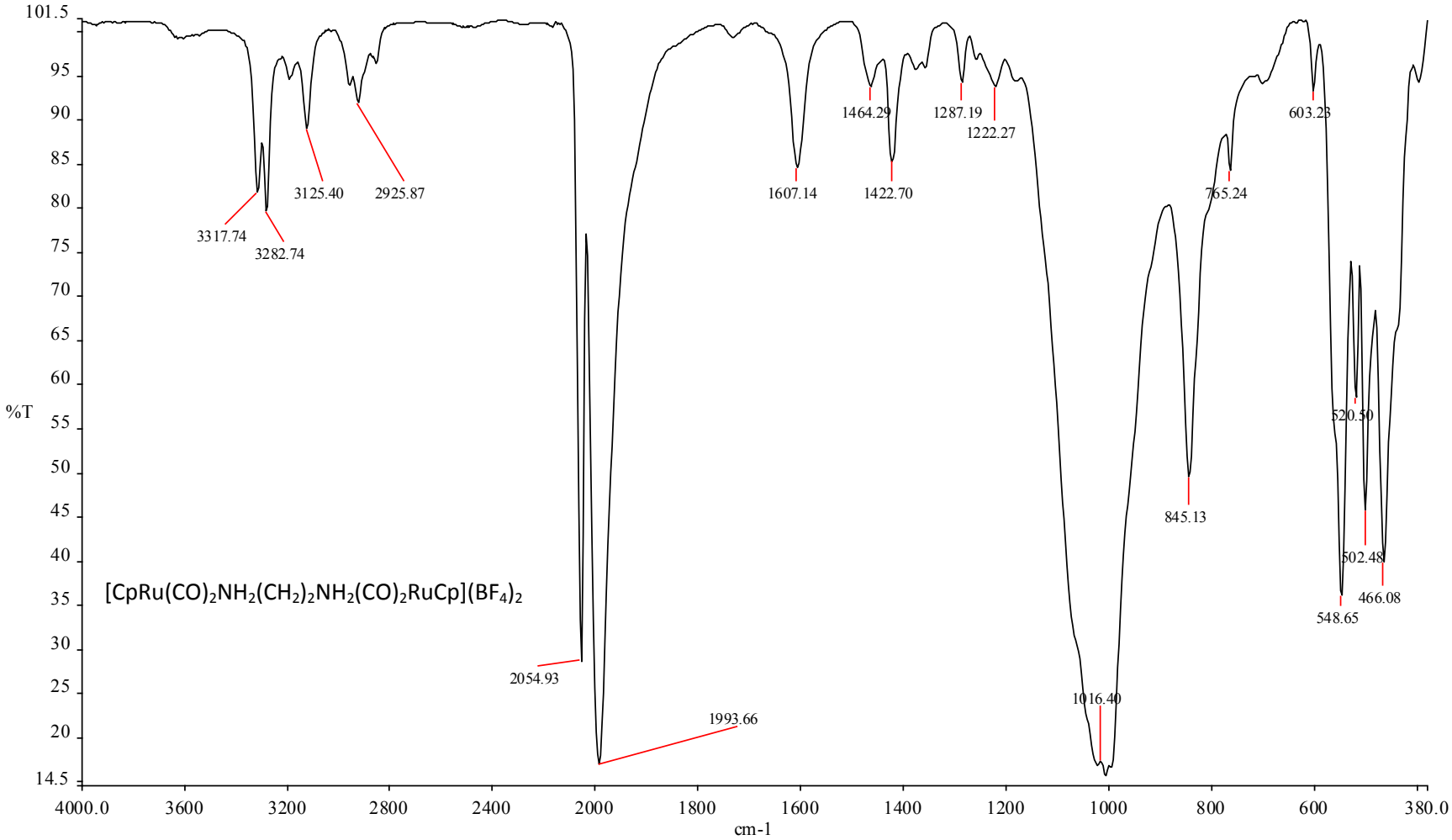

99.3
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
21.6
%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
380.0
cm-1
3116.67
3011.56
2948.92
2331.31
2136.91
2079.58
2030.37
1420.60
1365.08
1286.55
1030.87
854.82
602.60
520.58
553.52
494.79
541.06
464.14
439.46
391.57
[η5-C5(CH3)5Ru(CO)2NCCH3]BF

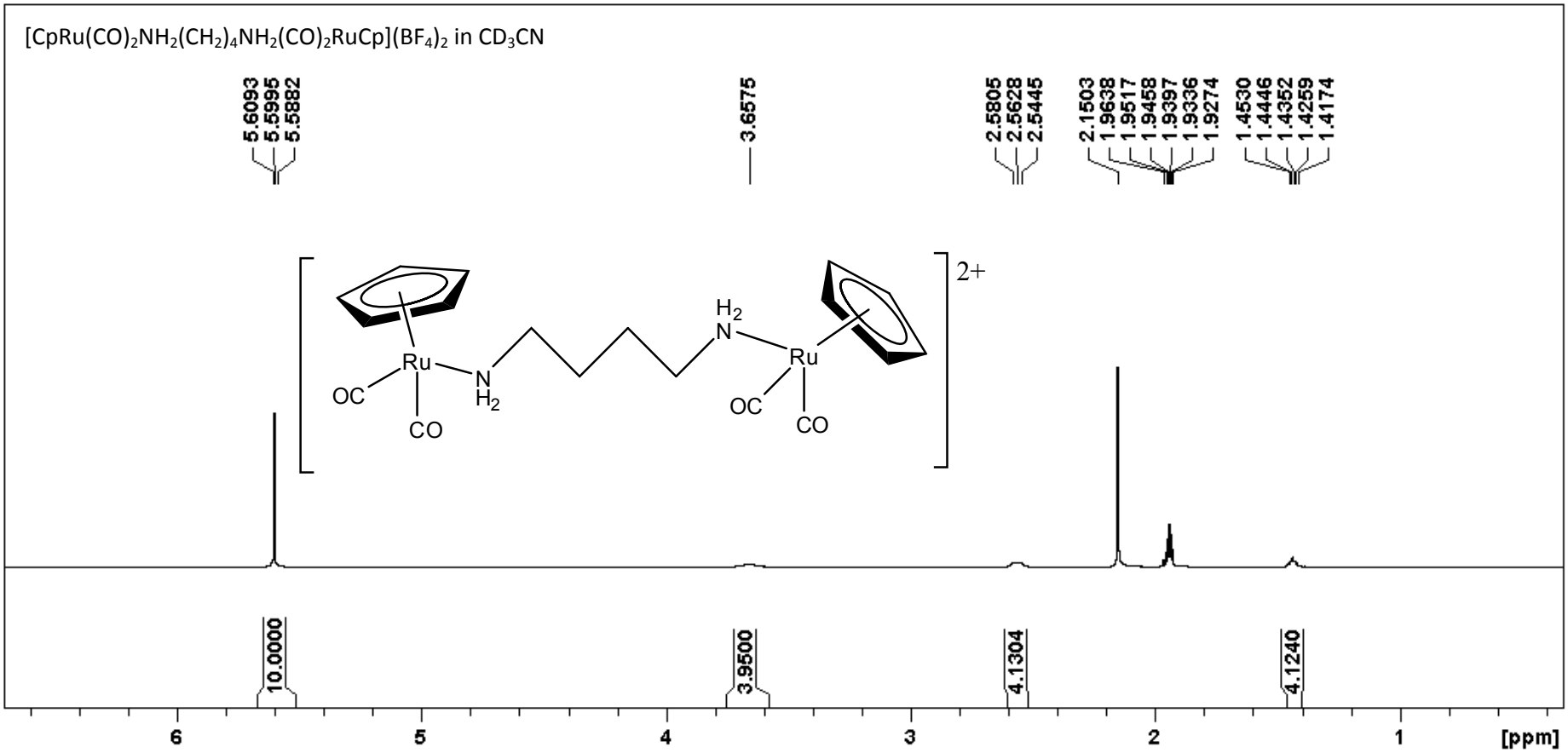

[CpRu(CO)2NH2(CH2)2NH2(CO)2RuCp](BF4)2 in CD3CN
5.6101
3.7228
2.6924
2.6853
2.6750
2.6657
2.6578
2.1774
1.9640
1.9519
1.9458
1.9398
1.9337
1.9276
2+
Ru
OC
CO
N
H2
H2
N
Ru
OC
CO
10.0000
4.0647
4.0673
6
5
4
3
2
1
[ppm]

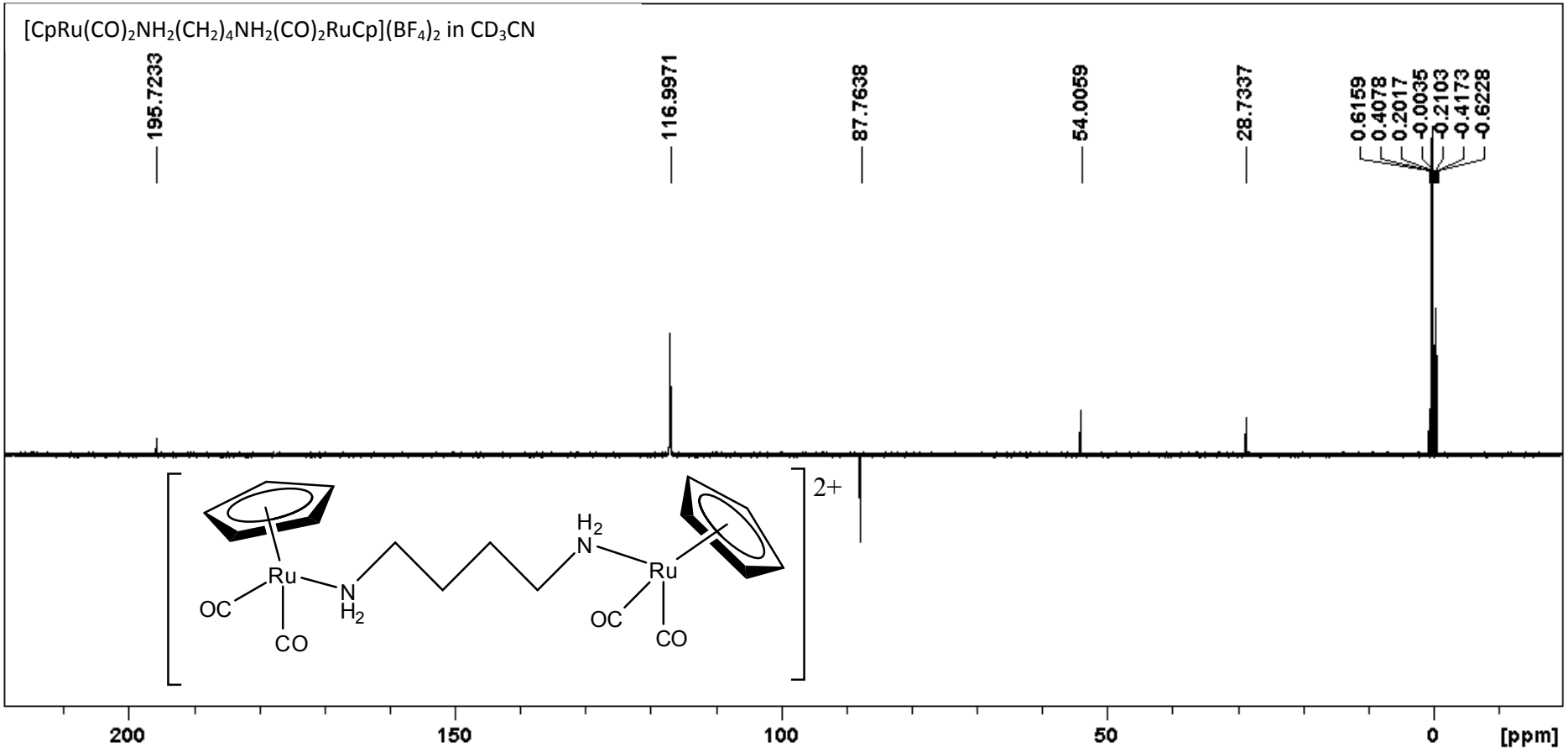

[CpRu(CO)2NH2(CH2)2NH2(CO)2RuCp](BF4)2 in CD3CN
195.4278
117.0181
87.7766
55.2029
0.6149
0.4080
0.2030
-0.0036
-0.2110
-0.4161
-0.6227
2+
Ru
OC
CO
N
H2
H2
N
Ru
OC
CO
200
150
100
50
0
[ppm]

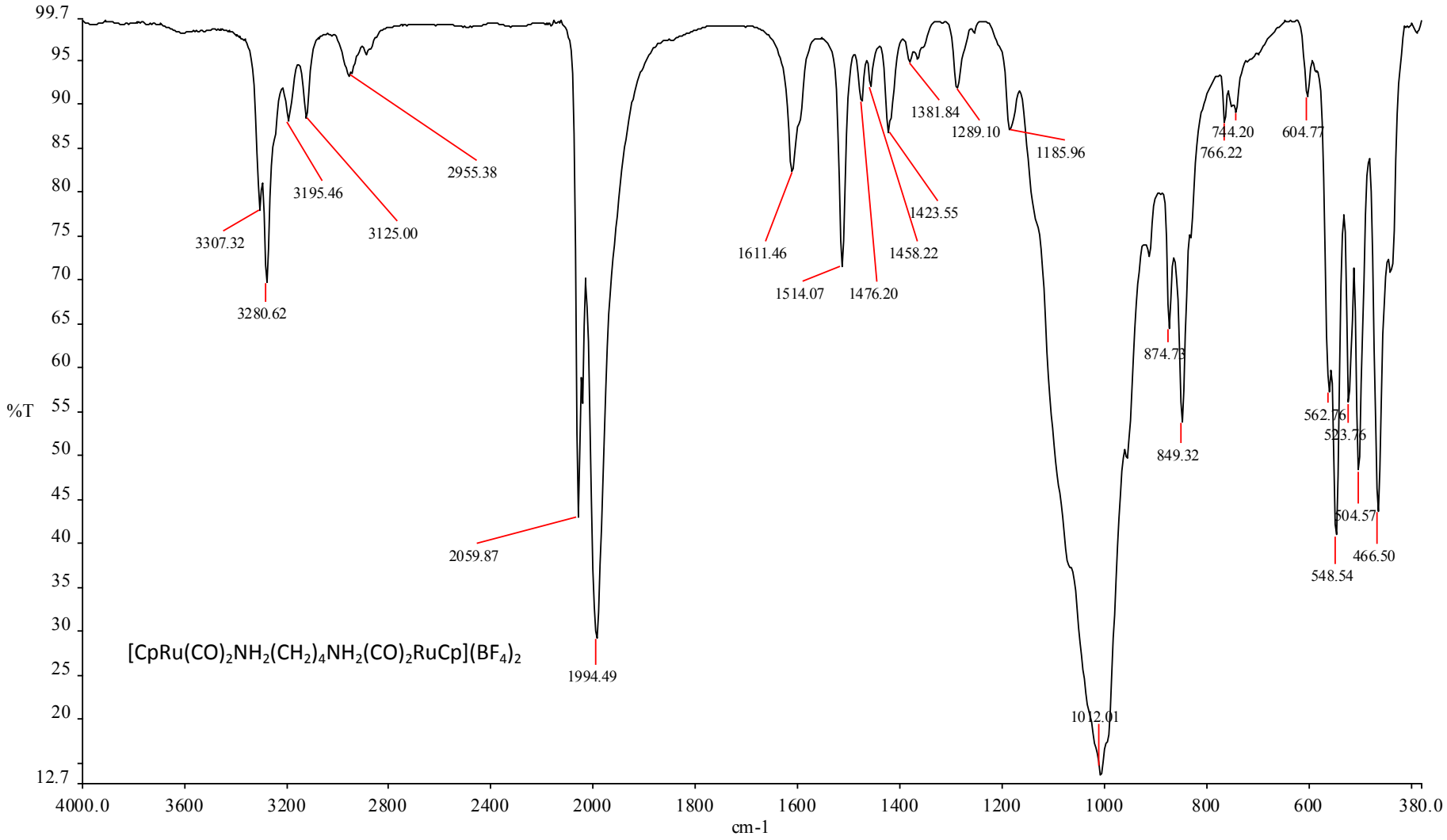

[CpRu(CO)2NH2(CH2)2NH2(CO)2RuCp](BF4)2 in D2O
5.6302
4.7999
2.7335
2.0397
10.0000
4.8039
6
5
4
3
2
1
[ppm]
Ru
OC
CO
N
H2
H2
N
Ru
OC
CO
2+

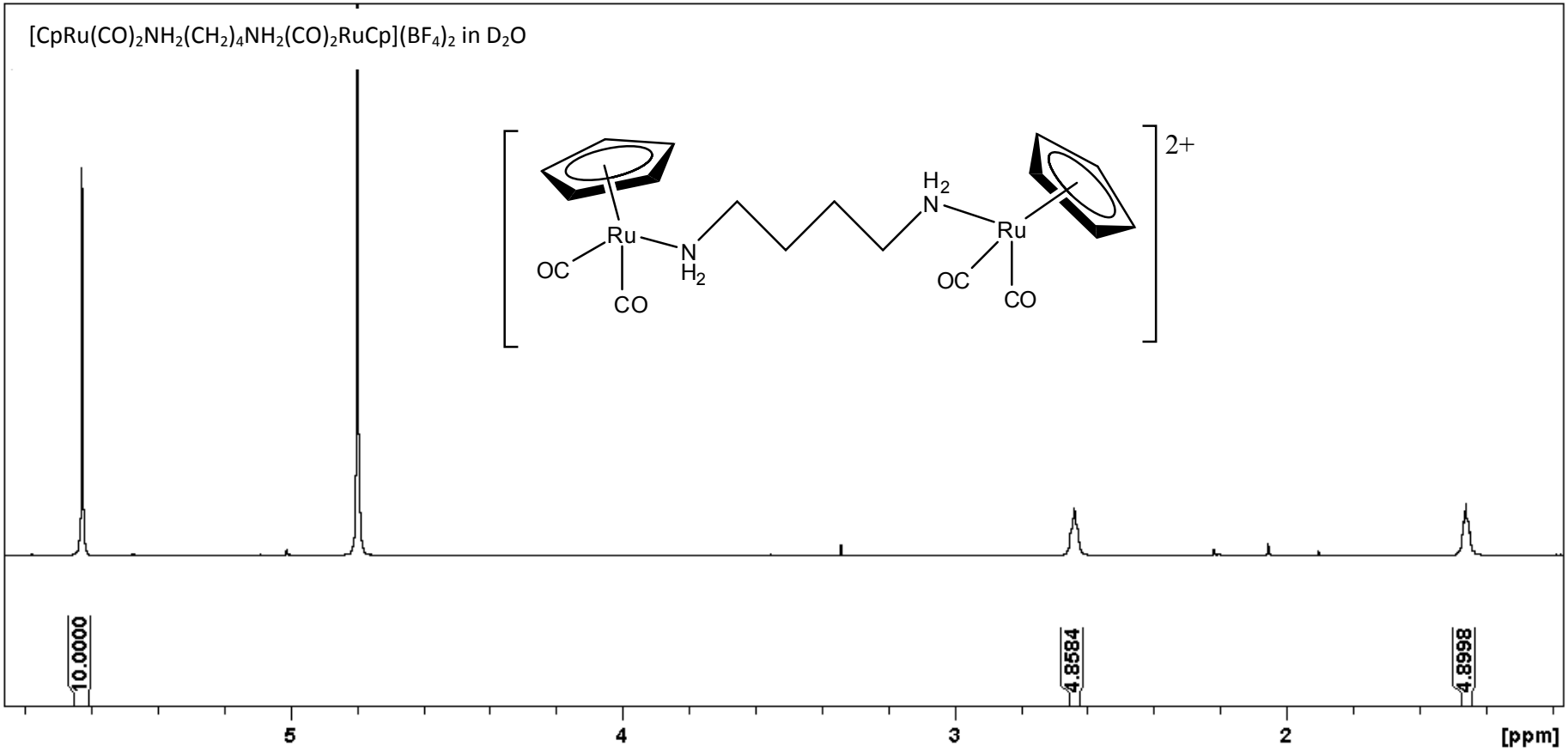

[CpRu(CO)2NH2(CH2)2NH2(CO)2RuCp](BF4)2 in D2O
195.7095
119.0682
87.6139
54.7314
0.8123
2+
Ru
OC
CO
N
H2
H2
N
Ru
OC
CO
200
150
100
50
0
[ppm]

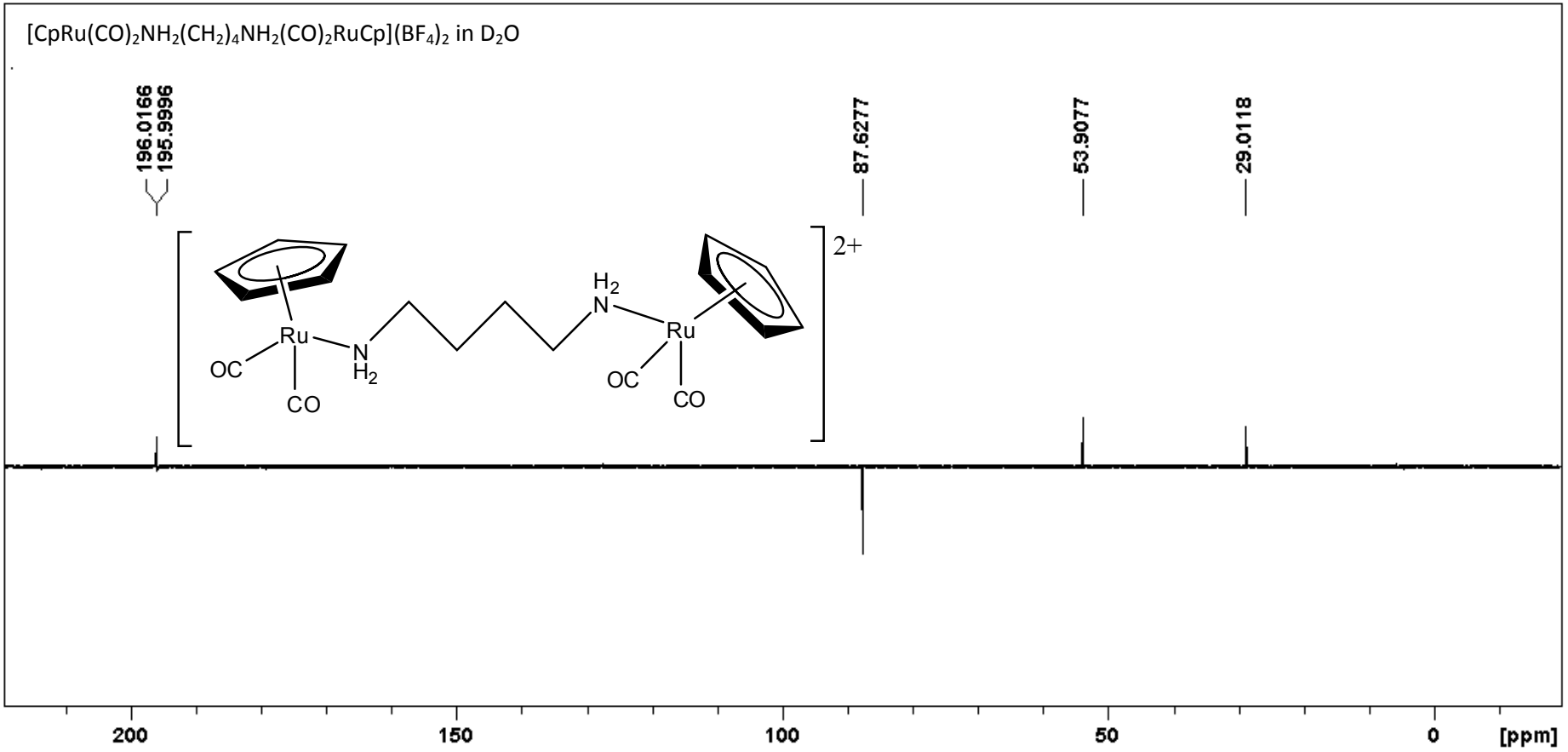

101.5
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
14.5
%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
380.0
cm-1
[CpRu(CO)2NH2(CH2)2NH2(CO)2RuCp](BF4)2
3317.74
3282.74
3125.40
2925.87
2054.93
1993.66
1607.14
1464.29
1422.70
1287.19
1222.27
1016.40
845.13
765.24
603.23
520.50
502.48
548.65
466.08

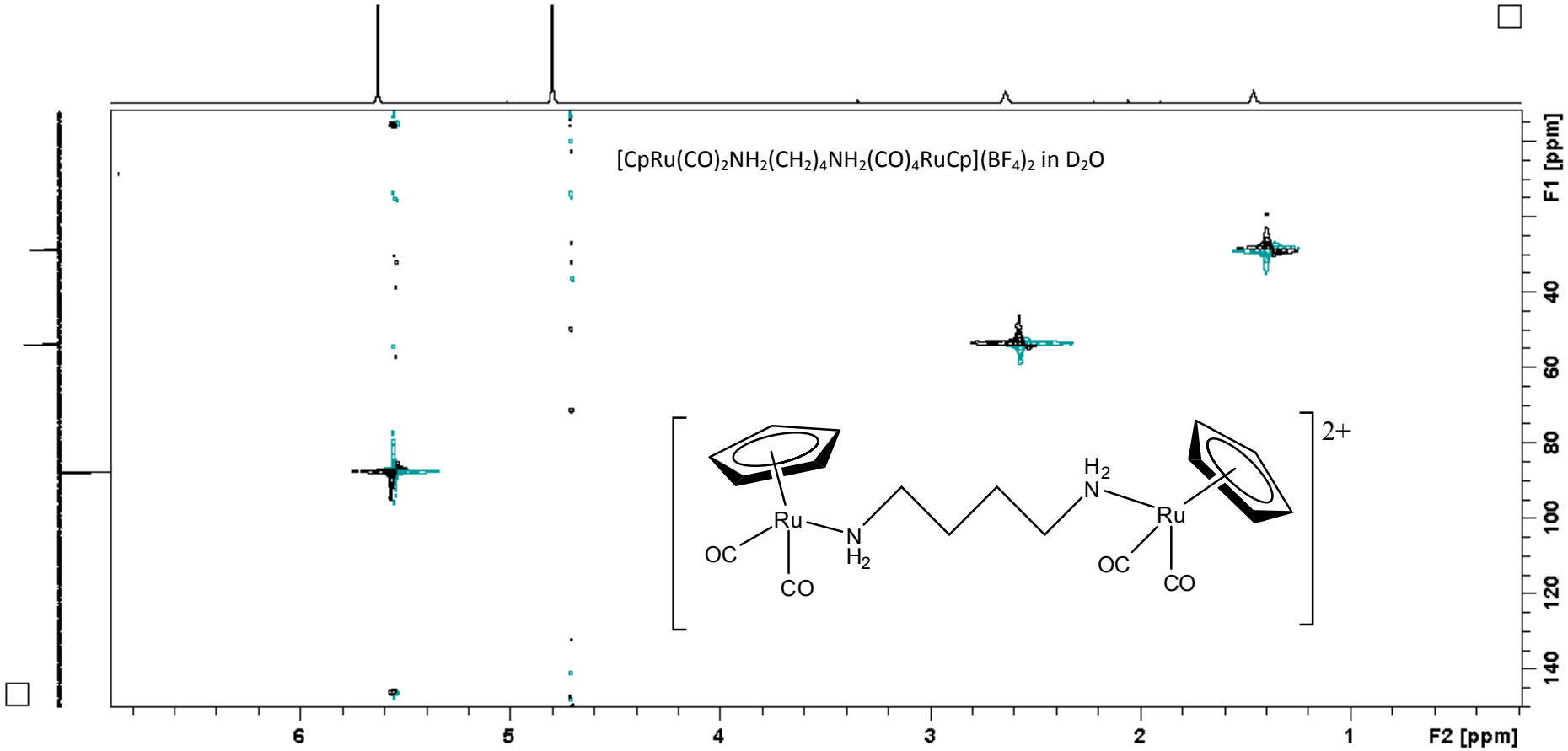

[CpRu(CO)2NH2(CH2)4NH2(CO)2RuCp](BF4)2 in CD3CN
5.6093
5.5995
5.5882
3.6575
2.5805
2.5628
2.5445
2.1503
1.9638
1.9517
1.9458
1.9397
1.9336
1.9274
1.4530
1.4446
1.4352
1.4259
1.4174
2+
Ru
OC
CO
N
H2
H2
N
Ru
OC
CO
10.0000
3.9500
4.1304
4.1240
6
5
4
3
2
1
[ppm]

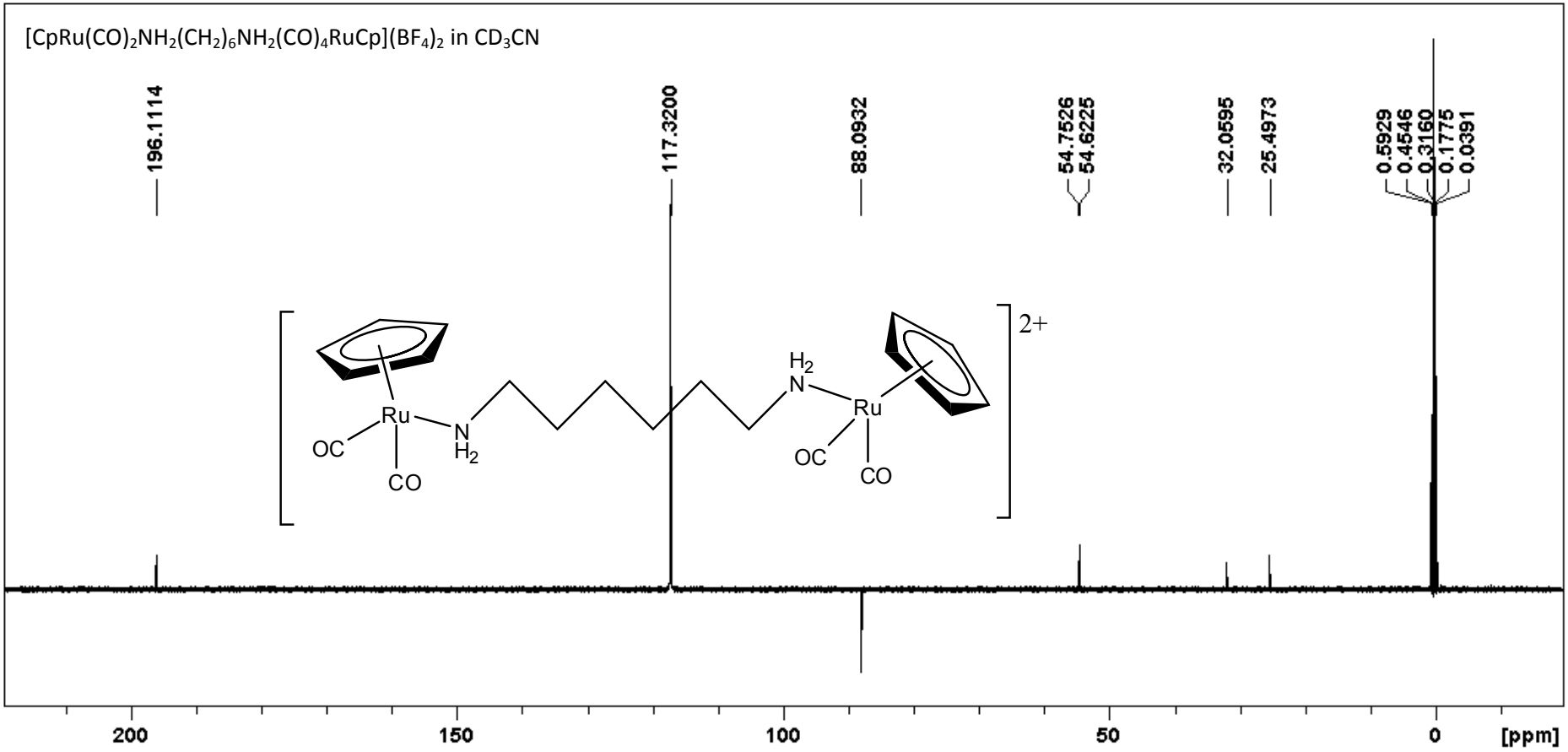

[CpRu(CO)2NH2(CH2)4NH2(CO)2RuCp](BF4)2 in CD3CN
195.7233
116.9971
87.7638
54.0059
28.7337
0.6159
0.4078
0.2017
-0.0035
-0.2103
-0.4173
-0.6228
2+
Ru
OC
CO
N
H2
H2
N
Ru
OC
CO
200
150
100
50
0
[ppm]

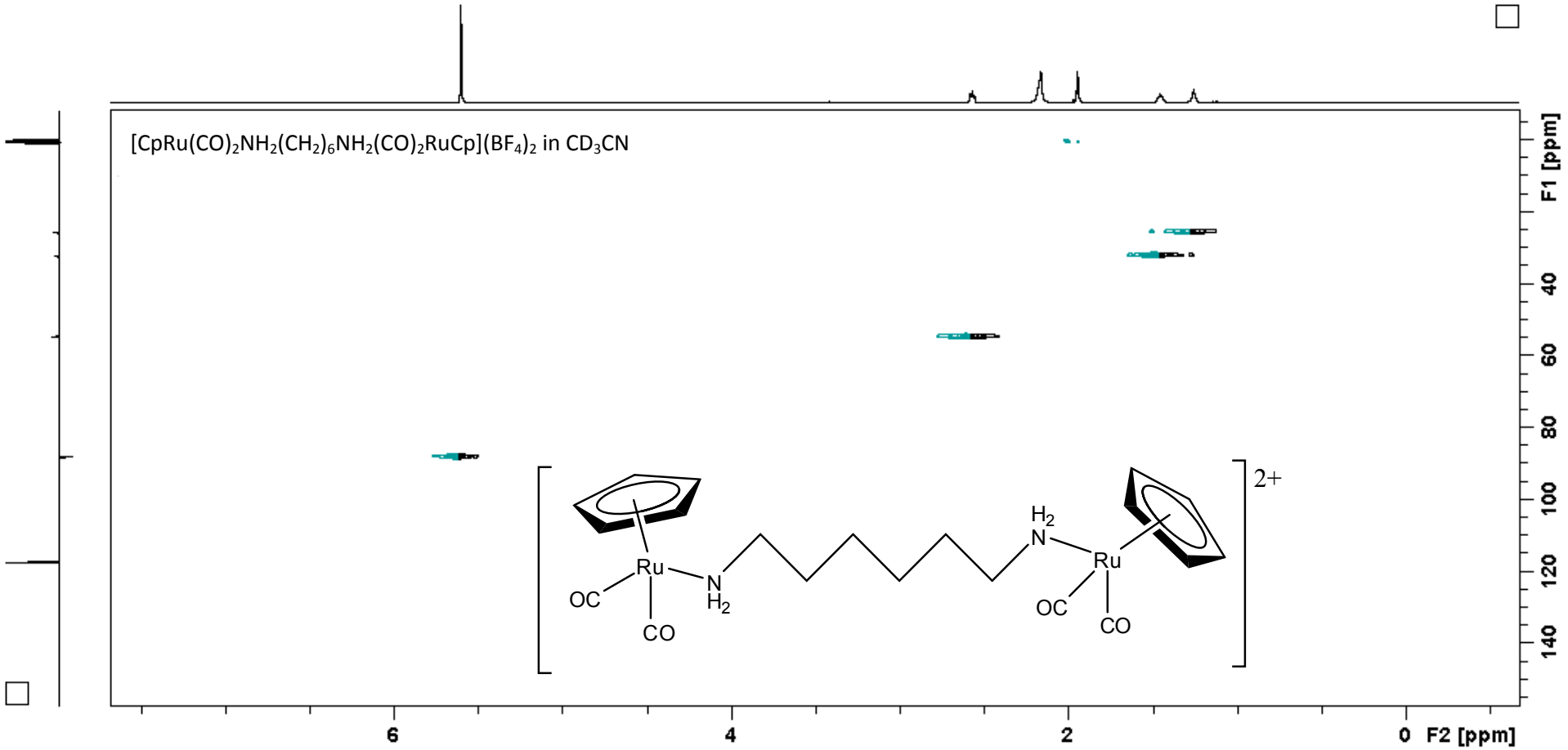

99.7
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
12.7
%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
380.0
cm-1
3307.32
3280.62
3195.46
3125.00
2955.38
2059.87
1994.49
1611.46
1514.07
1476.20
1458.22
1423.55
1381.84
1289.10
1185.96
1012.01
874.73
849.32
766.22
744.20
604.77
562.76
523.76
504.57
548.54
466.50
[CpRu(CO)2NH2(CH2)4NH2(CO)2RuCp](BF4)2

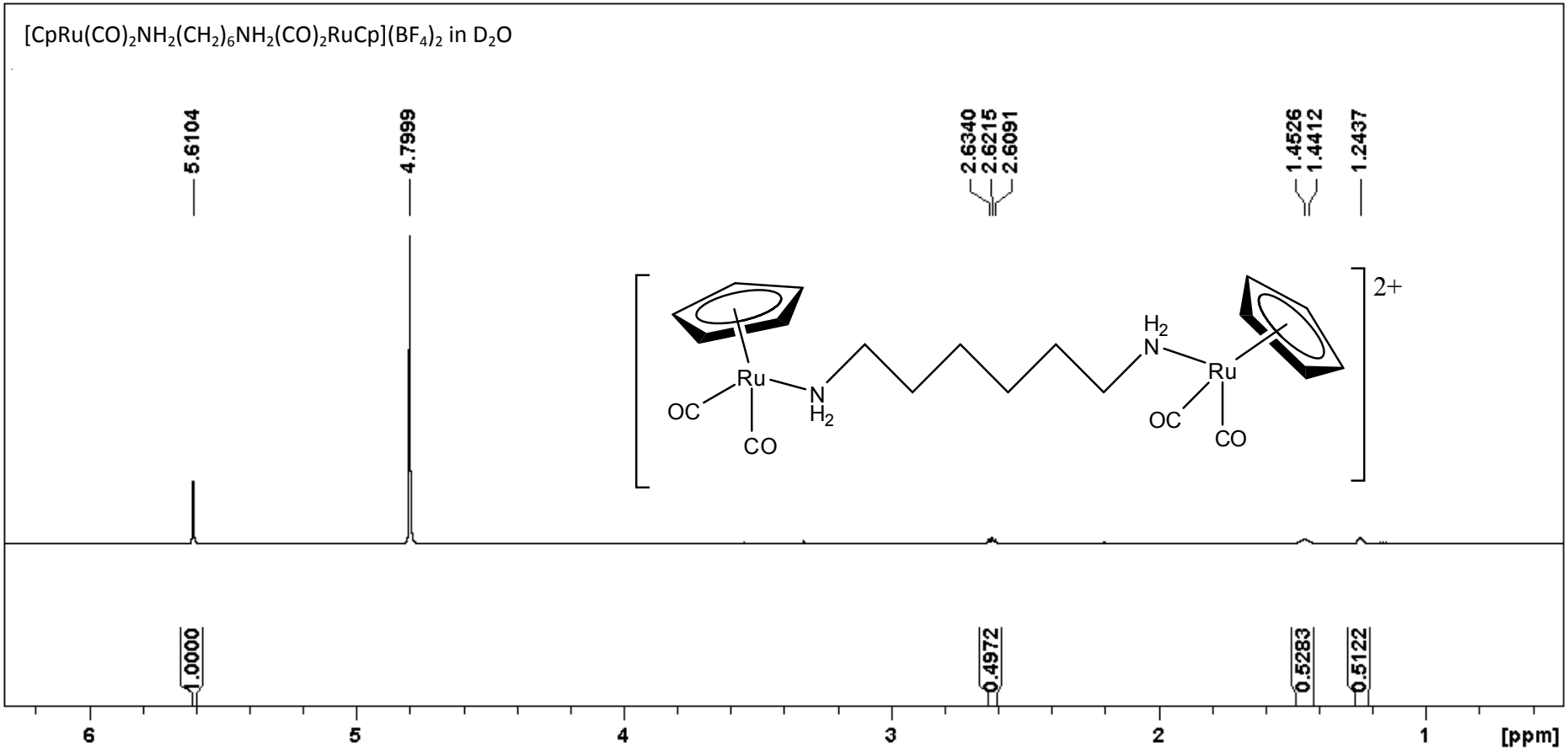

[CpRu(CO)2NH2(CH2)4NH2(CO)2RuCp](BF4)2 in D2O
2+
H2
N
Ru
OC
CO
N
H2
Ru
OC
CO
10.0000
4.8584
4.8998
5
4
3
2
[ppm]

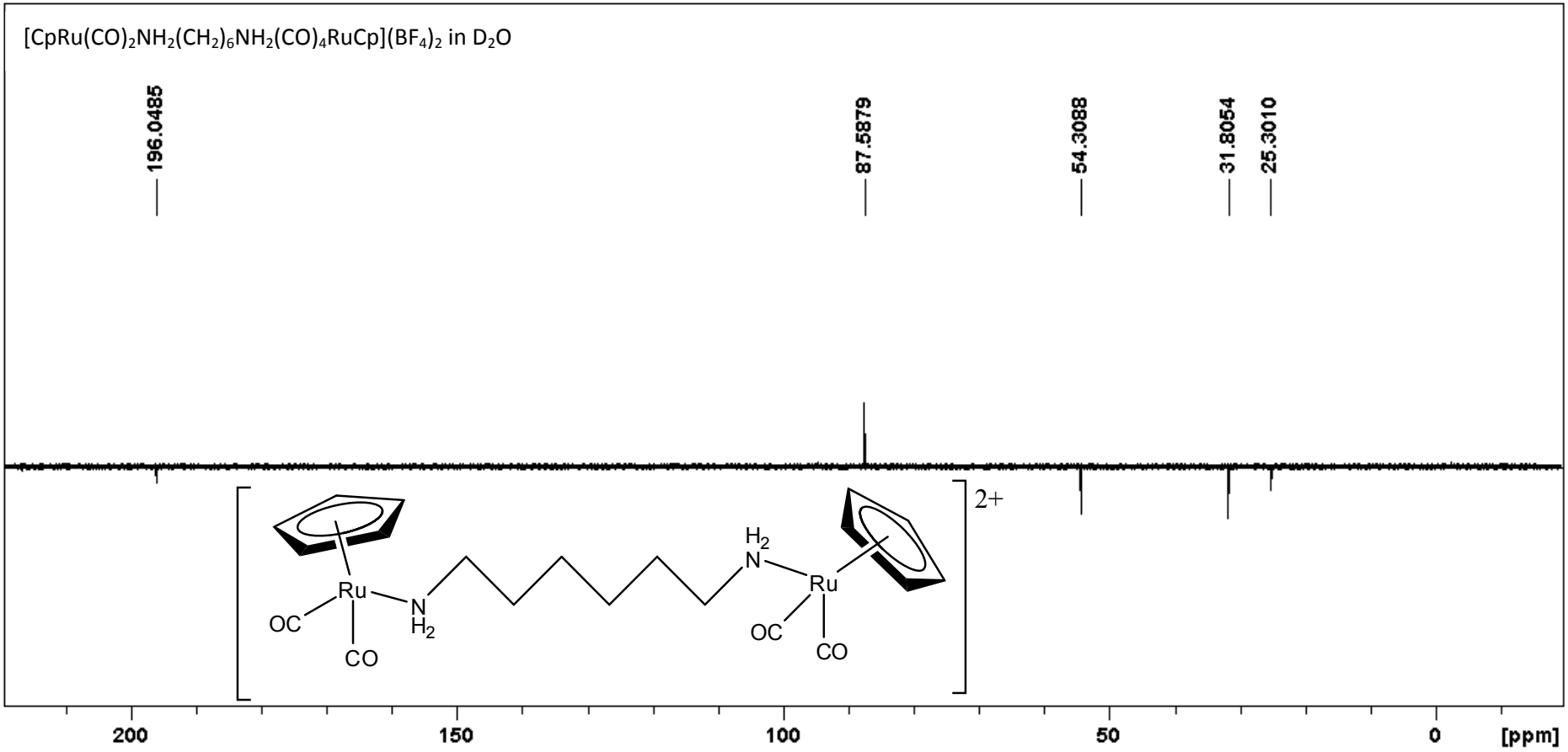

[CpRu(CO)2NH2(CH2)4NH2(CO)2RuCp](BF4)2 in D2O
196.0166
195.9996
87.6277
53.9077
29.0118
2+
Ru
OC
CO
N
H2
H2
N
Ru
OC
CO
200
150
100
50
0
[ppm]

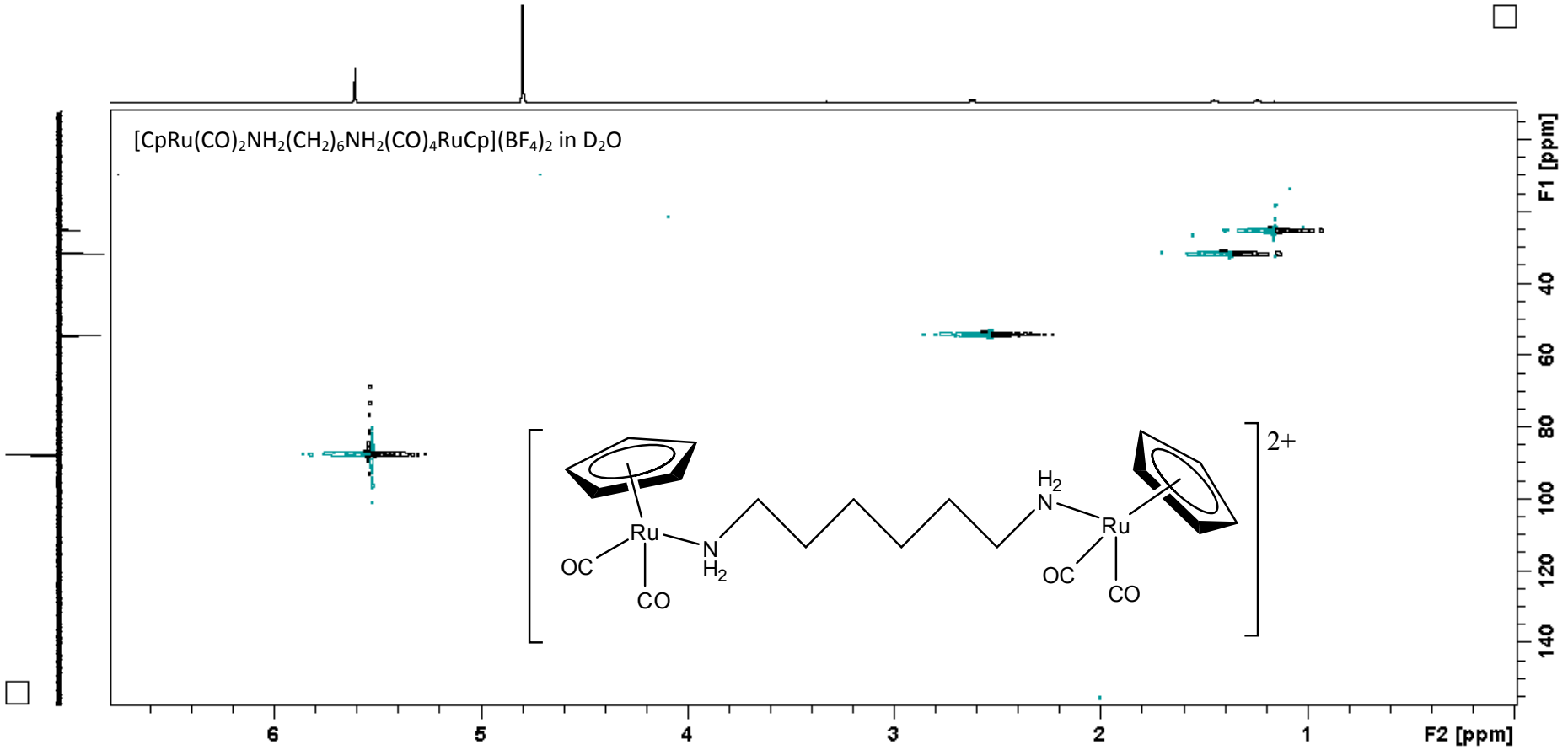

[CpRu(CO)2NH2(CH2)4NH2(CO)4RuCp](BF4)2 in D2O
F1 [ppm]
F2 [ppm]
2+

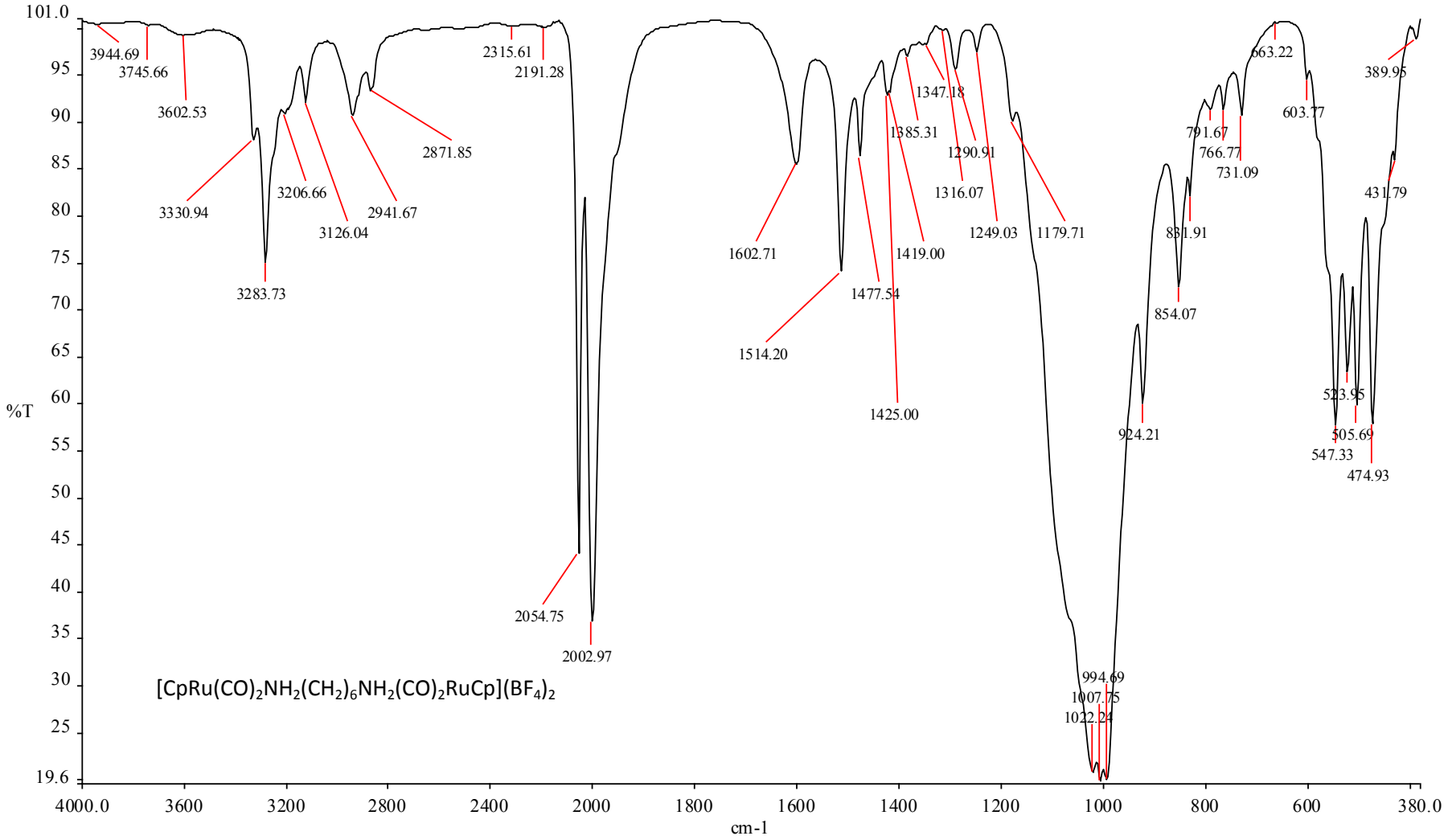

[CpRu(CO)2NH2(CH2)6NH2(CO)4RuCp](BF4)2 in CD3CN
196.1114
117.3200
88.0932
54.7526
54.6225
32.0595
25.4973
0.5929
0.4546
0.3160
0.1775
0.0391
Ru
OC
CO
N
H2
2+
200
150
100
50
0
[ppm]


[CpRu(CO)2NH2(CH2)6NH2(CO)2RuCp](BF4)2 in CD3CN
F1 [ppm]
F2 [ppm]
6
4
2
0
40
60
80
100
120
140
Ru
OC
CO
N
H2
2+

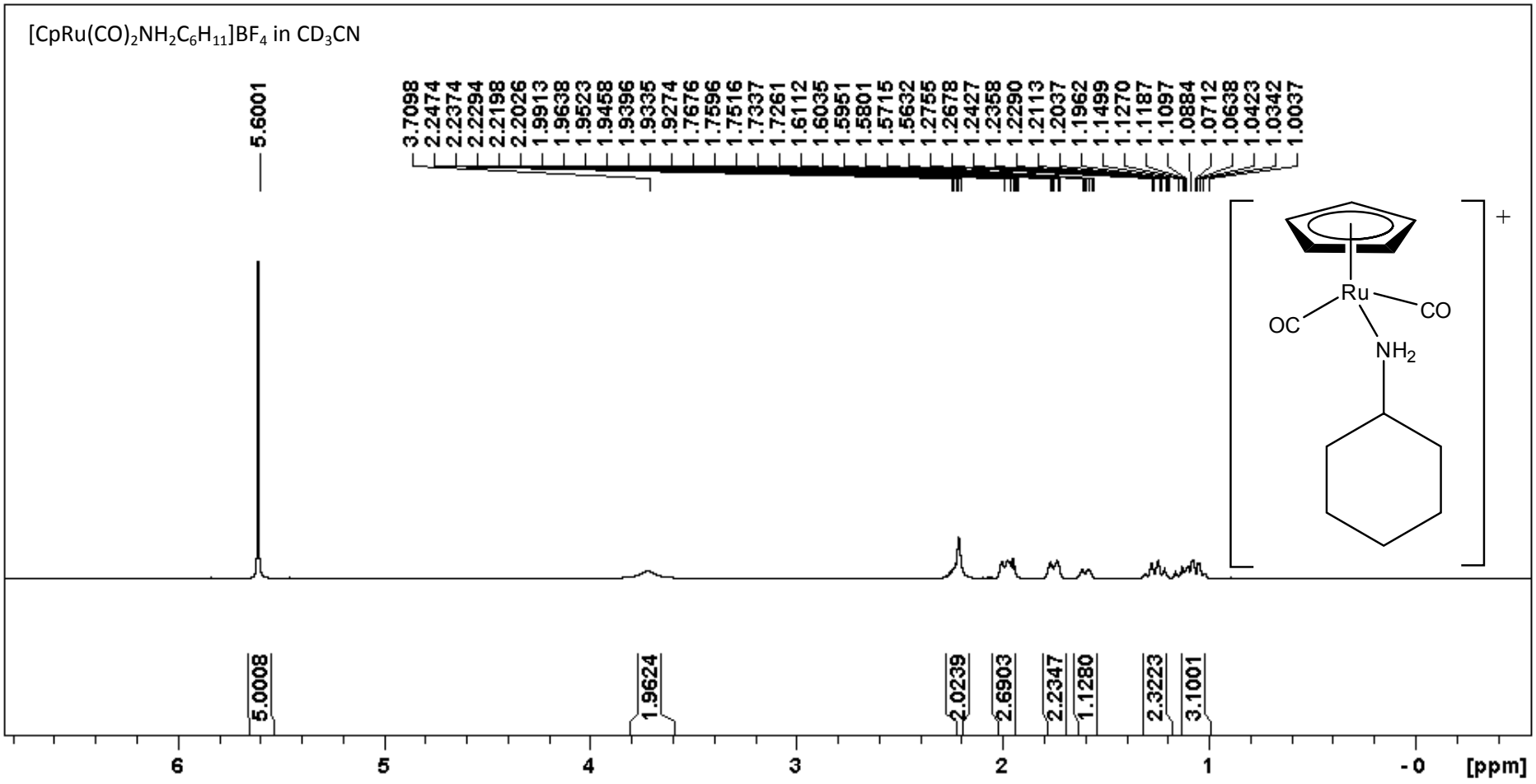

[CpRu(CO)2NH2(CH2)6NH2(CO)2RuCp](BF4)2 in D2O
5.6104
4.7999
2.6340
2.6215
2.6091
1.4526
1.4412
1.2437
2+
Ru
OC
CO
N
H2
1.0000
0.4972
0.5283
0.5122
6
5
4
3
2
1
[ppm]

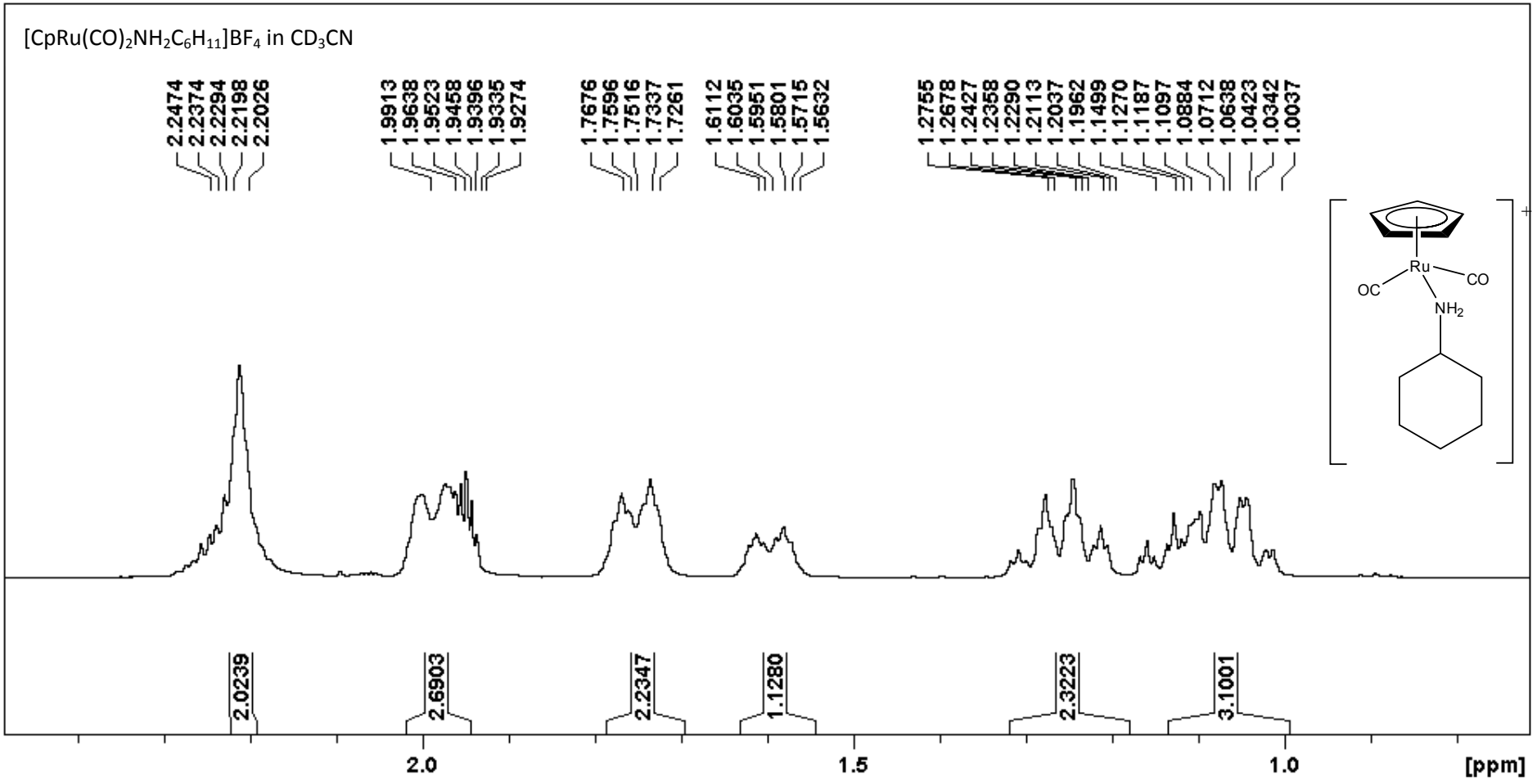

[CpRu(CO)2NH2(CH2)6NH2(CO)4RuCp](BF4)2 in D2O
196.0485
87.5879
54.3088
31.8054
25.3010
2+
Ru
OC
CO
N
H2
H2
N
Ru
OC
CO
200
150
100
50
0
[ppm]

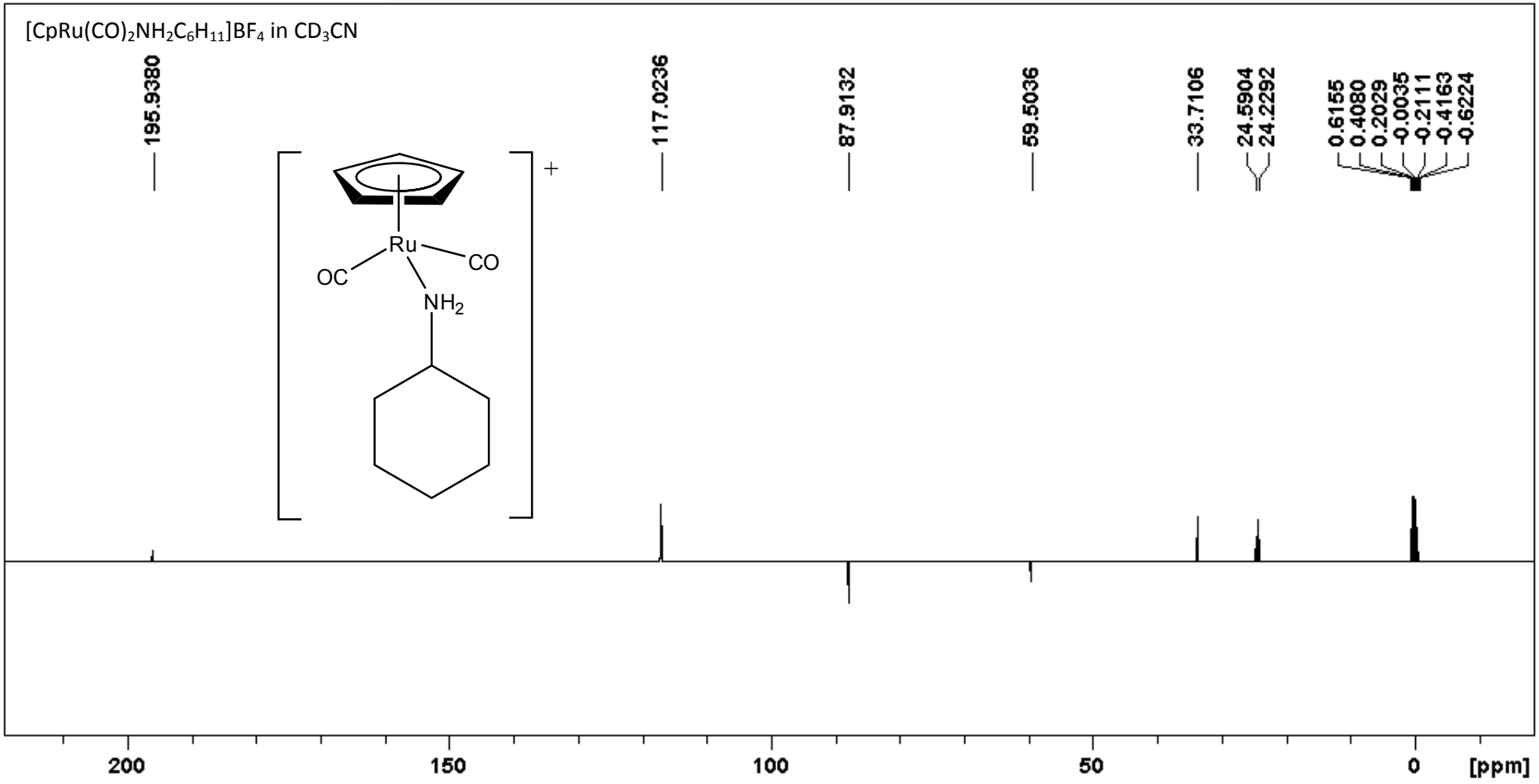

[CpRu(CO)2NH2(CH2)6NH2(CO)4RuCp](BF4)2 in D2O
F1 [ppm]
F2 [ppm]
2+
Ru
OC
CO
N
H2
H2
N
Ru
OC
CO

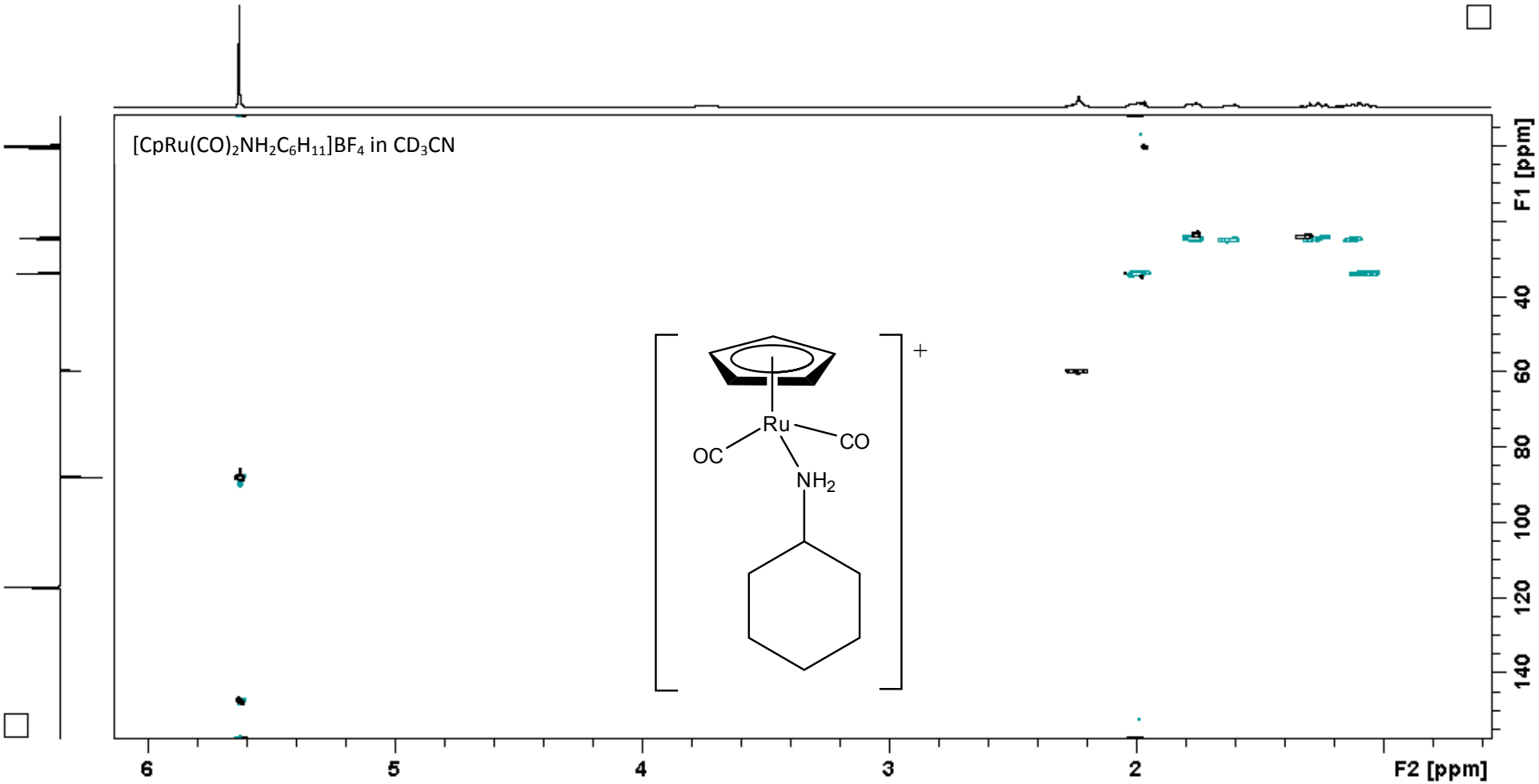

101.0
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
19.6
%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
380.0
cm-1
3944.69
3745.66
3602.53
3330.94
3283.73
3206.66
3126.04
2941.67
2871.85
2315.61
2191.28
2054.75
2002.97
1602.71
1514.20
1477.54
1425.00
1419.00
1385.31
1347.18
1316.07
1290.91
1249.03
1179.71
994.69
1007.75
1022.24
924.21
854.07
831.91
791.67
766.77
731.09
663.22
603.77
523.95
505.69
547.33
474.93
431.79
389.95
[CpRu(CO)2NH2(CH2)6NH2(CO)2RuCp](BF4)2

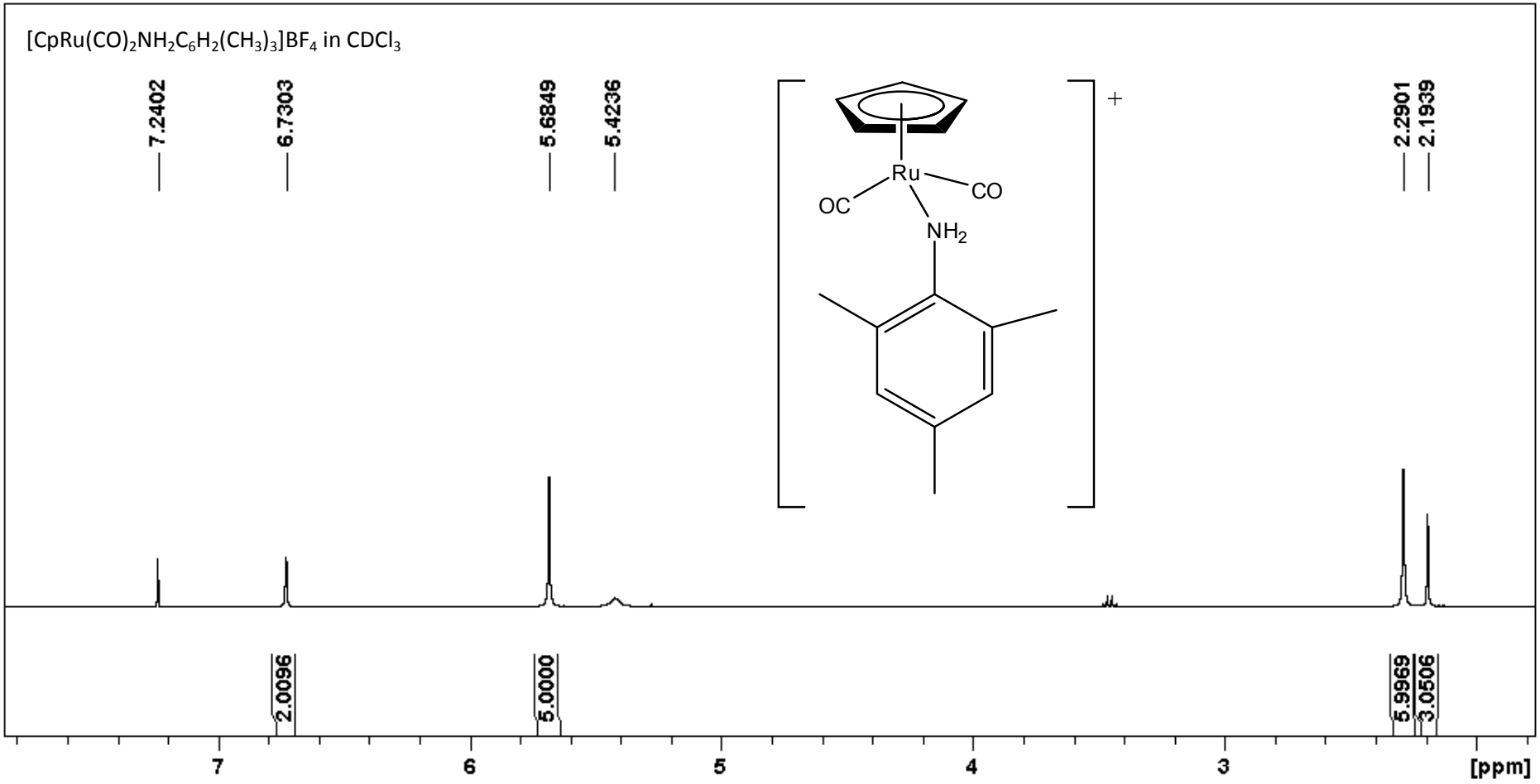
**SPECTRA DATA PERTAINING TO CHAPTER 6**

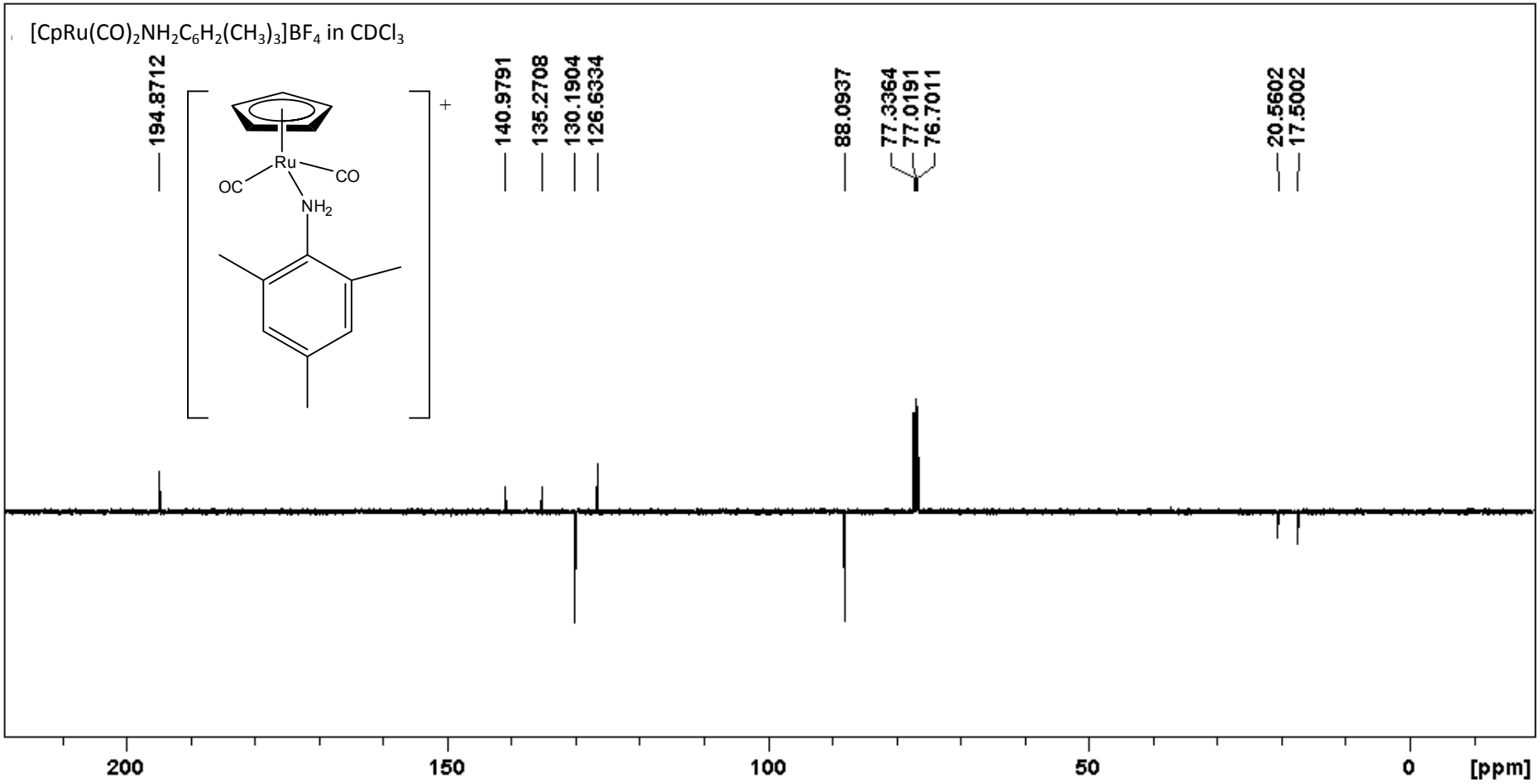


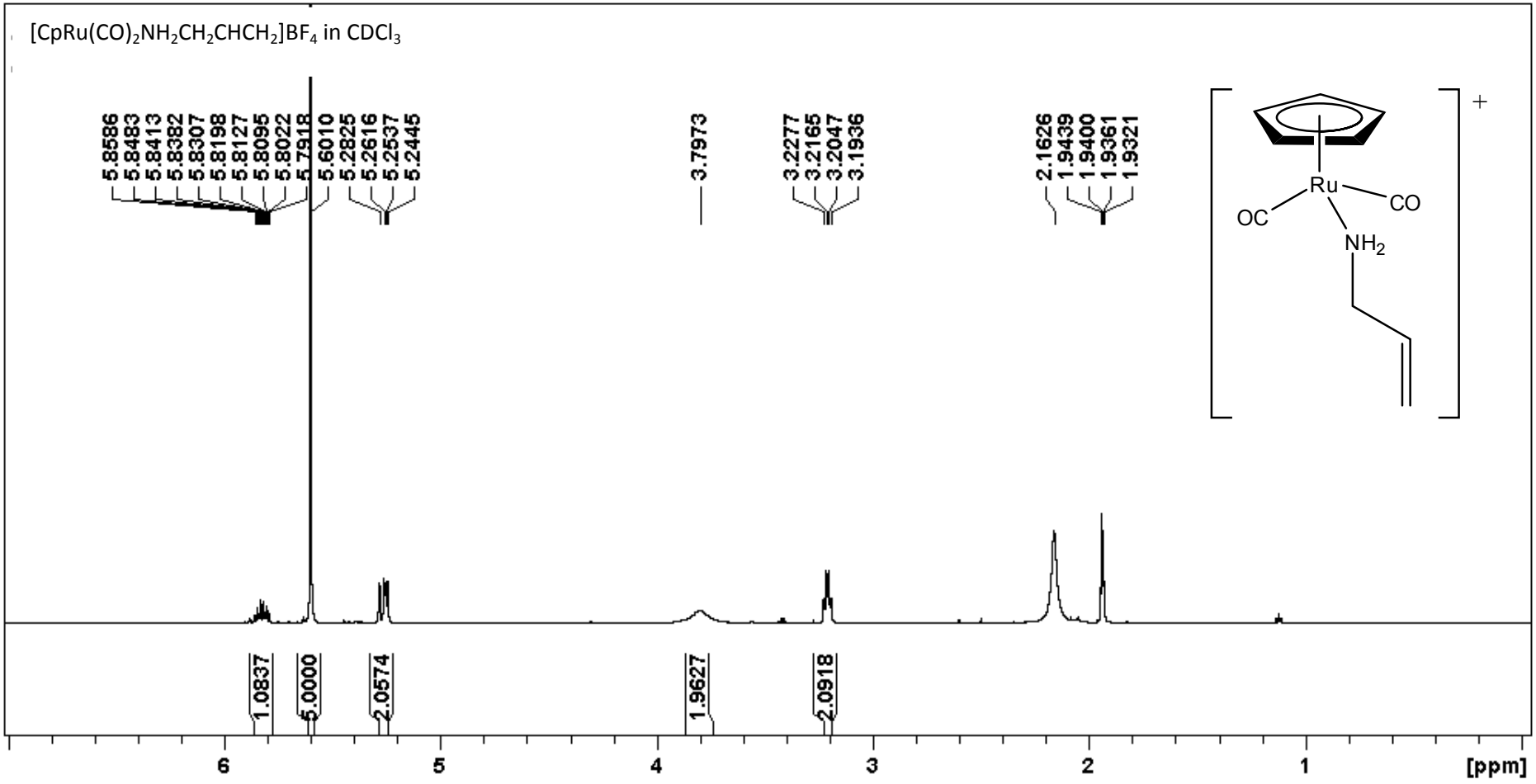

[CpRu(CO)2NH2C6H11]BF4 in CD3CN
2.2474
2.2374
2.2294
2.2198
2.2026
1.9913
1.9638
1.9523
1.9458
1.9396
1.9335
1.9274
1.7676
1.7596
1.7516
1.7337
1.7261
1.6112
1.6035
1.5951
1.5801
1.5715
1.5632
1.2755
1.2678
1.2427
1.2358
1.2290
1.2113
1.2037
1.1962
1.1499
1.1270
1.1187
1.1097
1.0884
1.0712
1.0638
1.0423
1.0342
1.0037
Ru
OC
CO
NH2
2.0239
2.6903
2.2347
1.1280
2.3223
3.1001
2.0
1.5
1.0
[ppm]

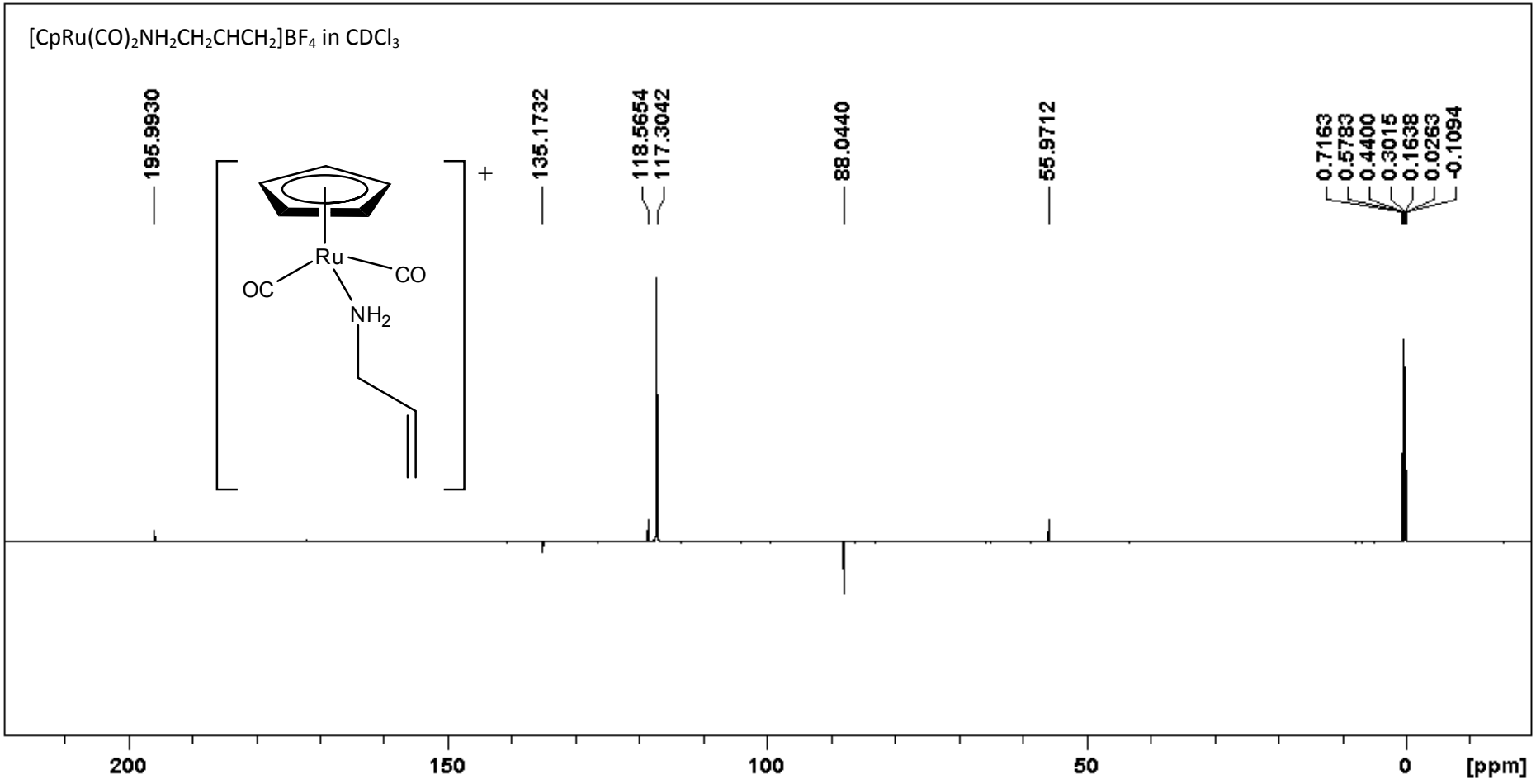

[CpRu(CO)2NH2C6H11]BF4 in CD3CN
195.9380
117.0236
87.9132
59.5036
33.7106
24.5904
24.2292
0.6155
0.4080
0.2029
-0.0035
-0.2111
-0.4163
-0.6224
Ru
CO
OC
NH2
+
200
150
100
50
0
[ppm]

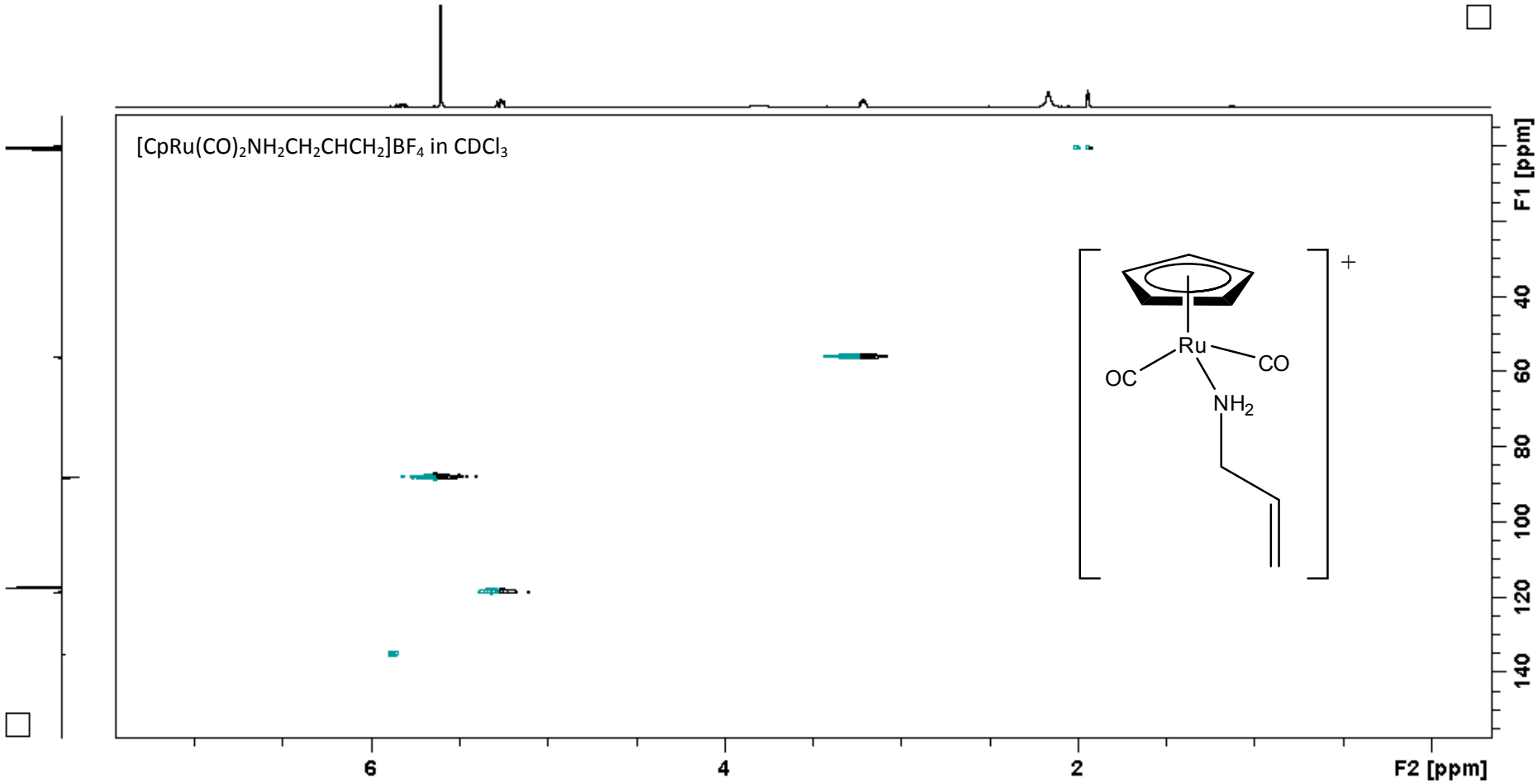

[CpRu(CO)2NH2C6H11]BF4 in CD3CN
Ru
OC
CO
NH2
+
F1 [ppm]
40
60
80
100
120
140
6
5
4
3
2
F2 [ppm]

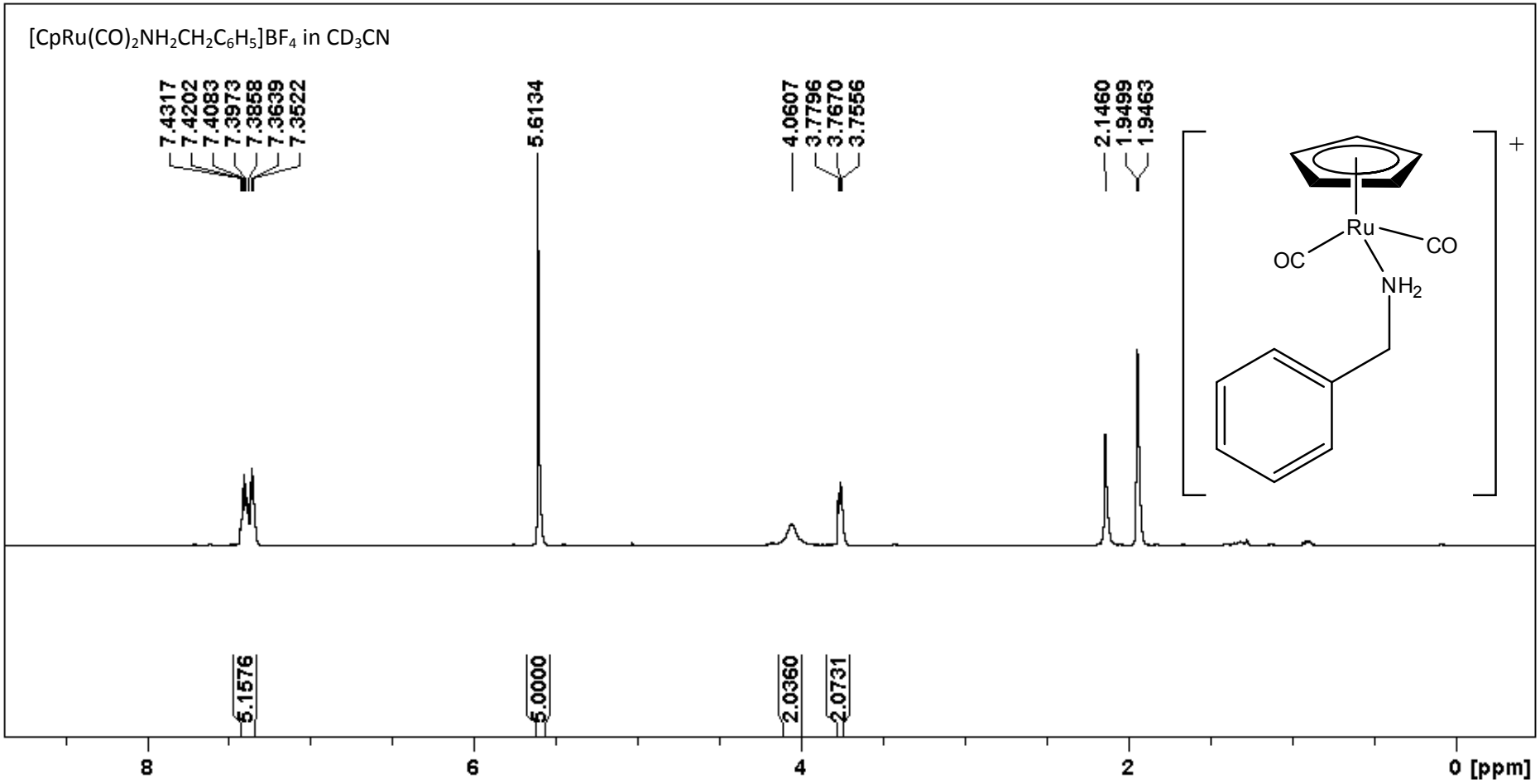

[CpRu(CO)2NH2C6H2(CH3)3]BF4 in CDCl3
7.2402
6.7303
5.6849
5.4236
2.2901
2.1939
Ru
CO
OC
NH2
+
2.0096
5.0000
5.9969
3.0506
7
6
5
4
3
[ppm]

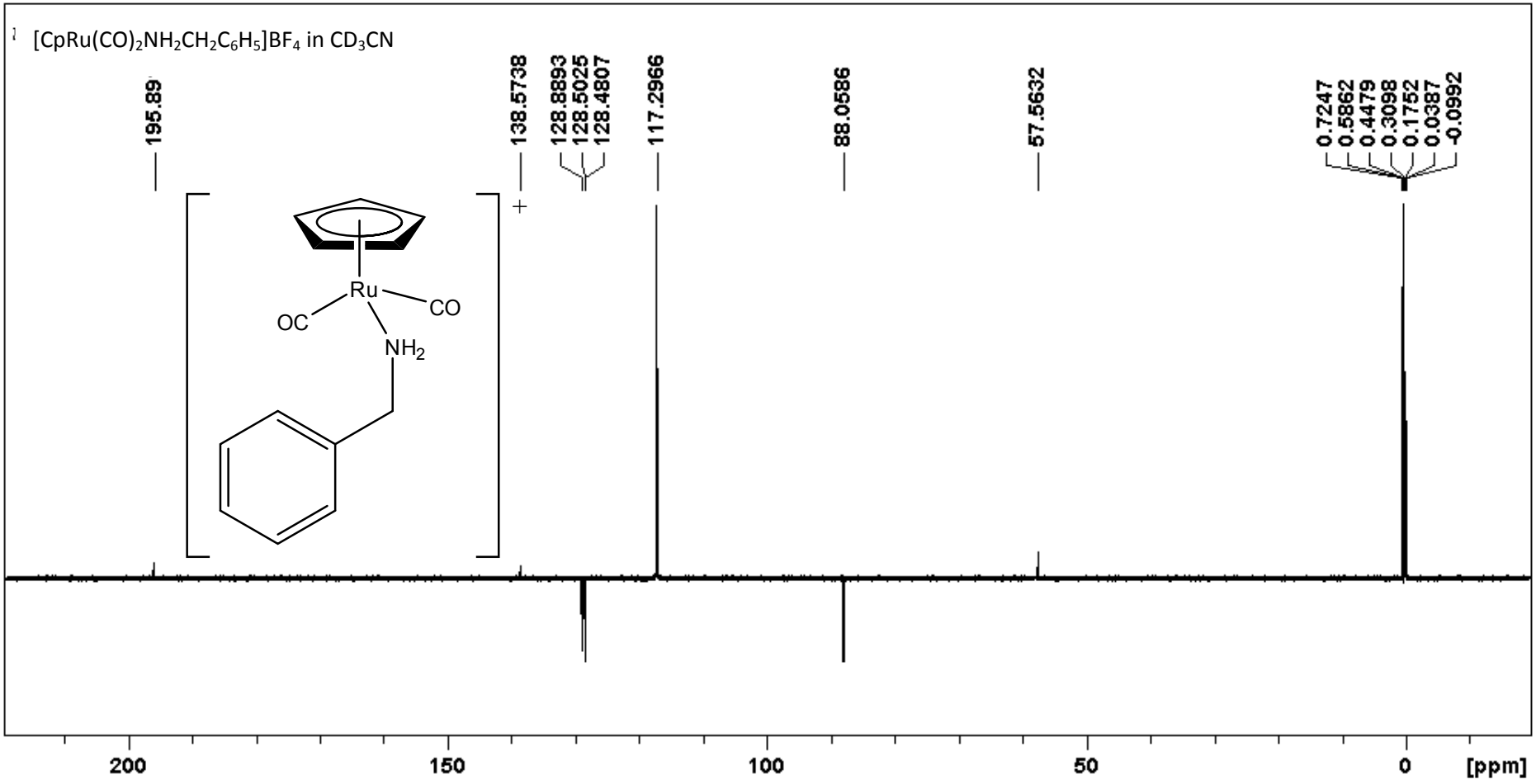

[CpRu(CO)2NH2C6H2(CH3)3]BF4 in CDCl3
194.8712
140.9791
135.2708
130.1904
126.6334
88.0937
77.3364
77.0191
76.7011
20.5602
17.5002
Ru
OC
CO
NH2
+
200
150
100
50
0
[ppm]

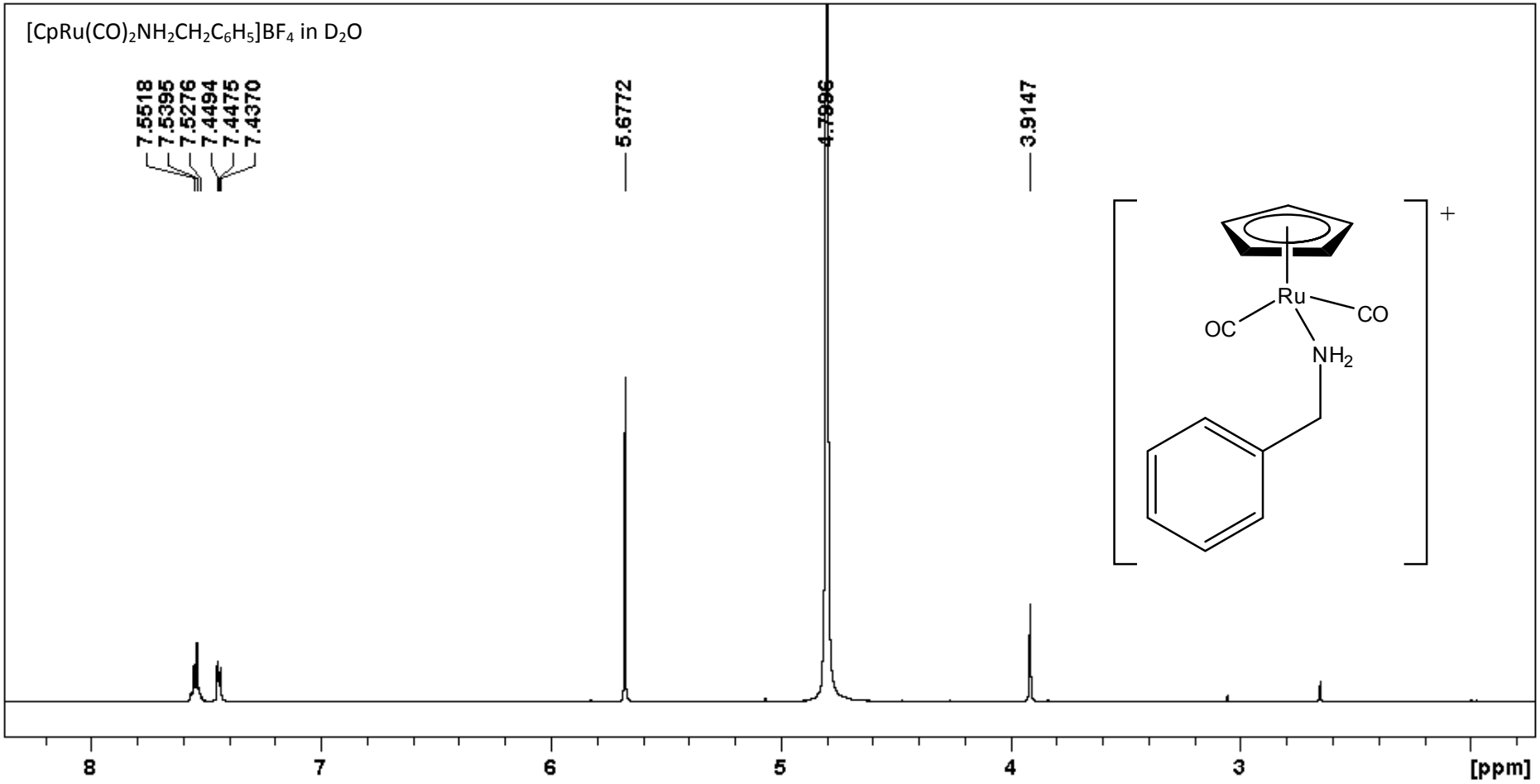

[CpRu(CO)2NH2CH2CHCH2]BF4 in CDCl3
5.8586
5.8483
5.8413
5.8382
5.8307
5.8198
5.8127
5.8095
5.8022
5.7918
5.6010
5.2825
5.2616
5.2537
5.2445
3.7973
3.2277
3.2165
3.2047
3.1936
2.1626
1.9439
1.9400
1.9361
1.9321
1.0837
5.0000
2.0574
1.9627
2.0918
6
5
4
3
2
1
[ppm]
Ru
OC
CO
NH2
+

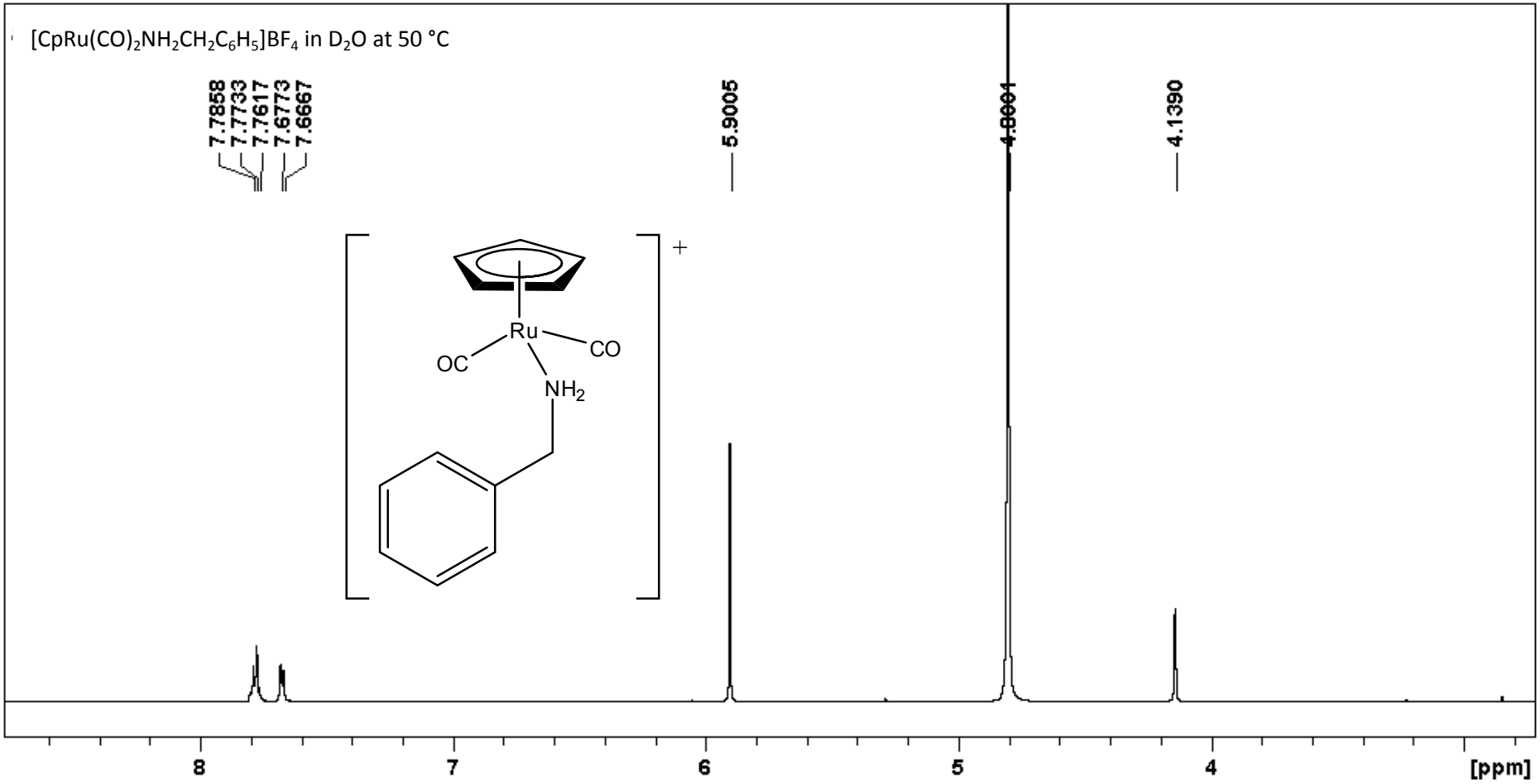

[CpRu(CO)2NH2CH2CHCH2]BF4 in CDCl3
195.9930
135.1732
118.5654
117.3042
88.0440
55.9712
0.7163
0.5783
0.4400
0.3015
0.1638
0.0263
-0.1094
Ru
CO
OC
NH2
+
200
150
100
50
0
[ppm]

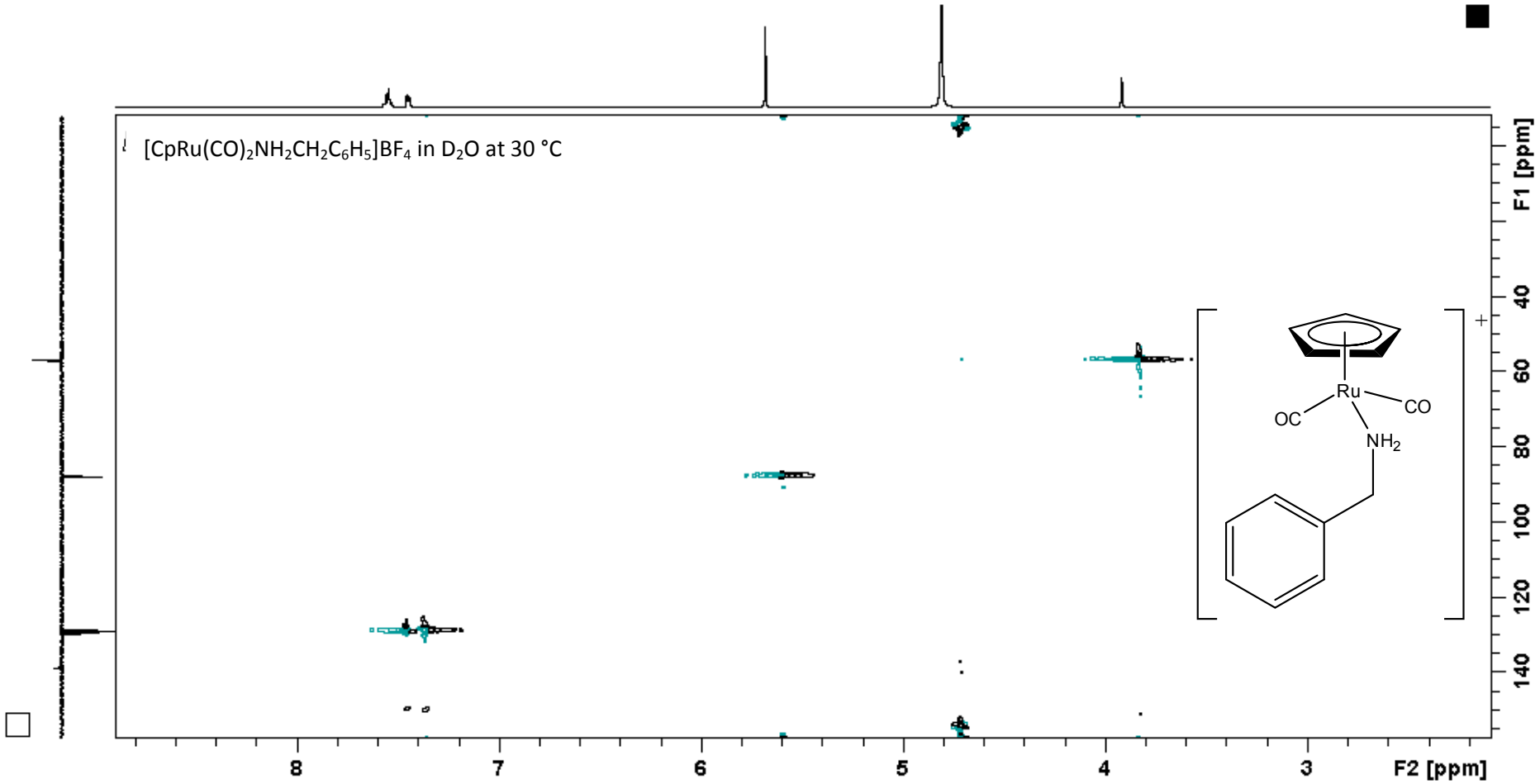

[CpRu(CO)2NH2CH2CHCH2]BF4 in CDCl3
Ru
CO
OC
NH2
+
F1 [ppm]
40
60
80
100
120
140
6
4
2
F2 [ppm]

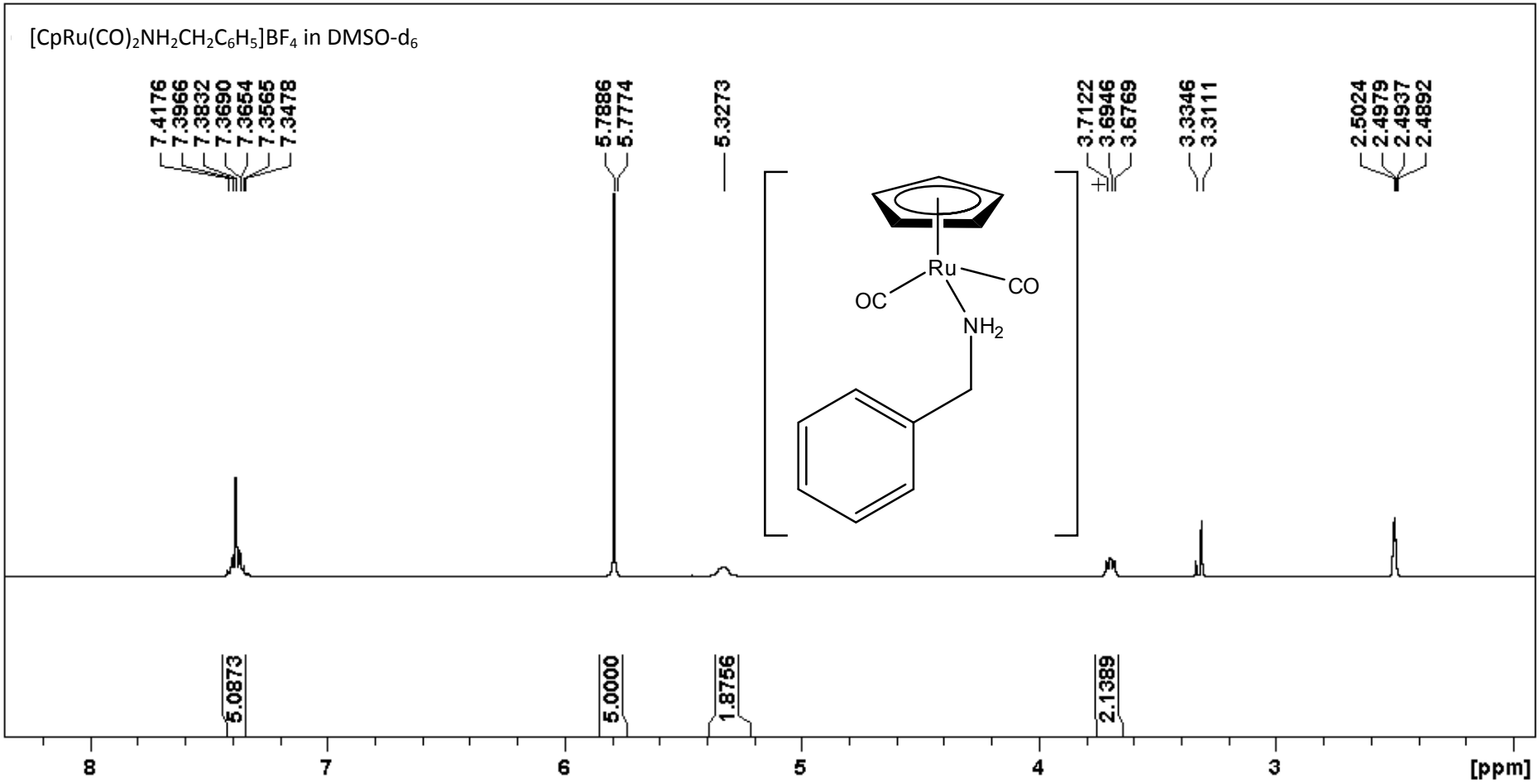

[CpRu(CO)2NH2CH2C6H5]BF4 in CD3CN
7.4317
7.4202
7.4083
7.3973
7.3858
7.3639
7.3522
5.6134
4.0607
3.7796
3.7670
3.7556
2.1460
1.9499
1.9463
Ru
OC
CO
NH2
+
5.1576
5.0000
2.0360
2.0731
8
6
4
2
0 [ppm]

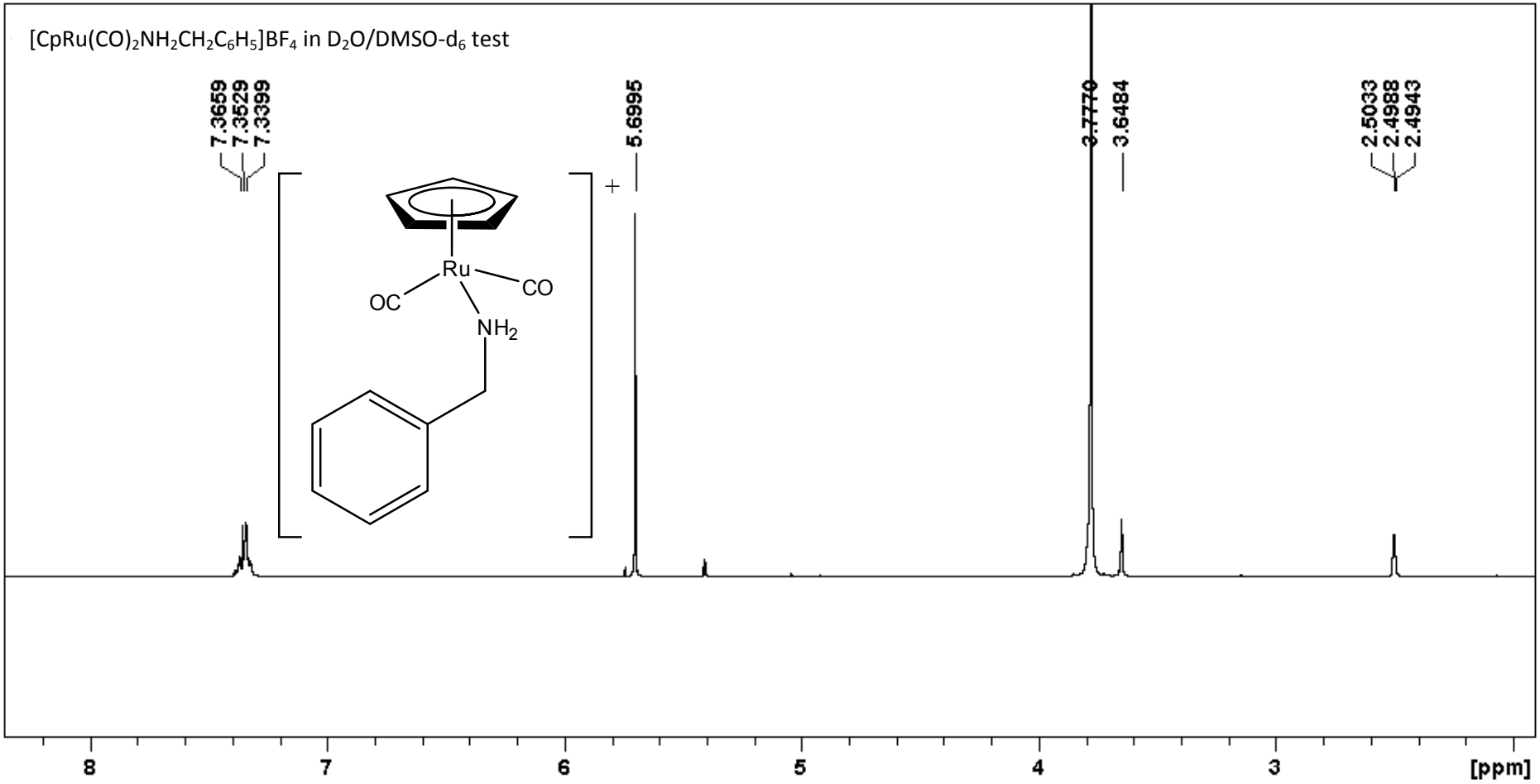

[CpRu(CO)2NH2CH2C6H5]BF4 in CD3CN
195.89
138.5738
128.8893
128.5025
128.4807
117.2966
88.0586
57.5632
0.7247
0.5862
0.4479
0.3098
0.1752
0.0387
-0.0992
Ru
OC
CO
NH2
200
150
100
50
0
[ppm]

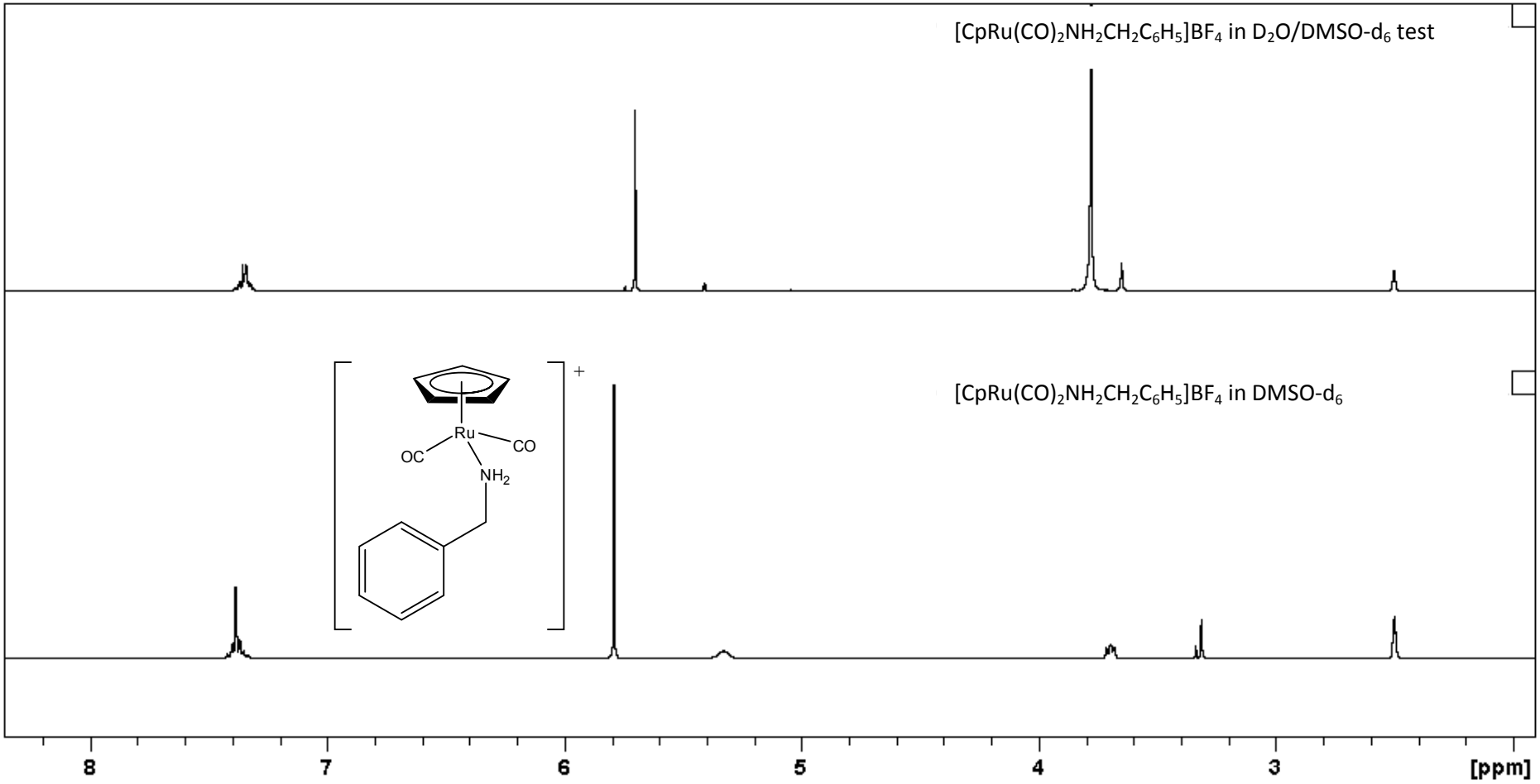

[CpRu(CO)2NH2CH2C6H5]BF4 in D2O
7.5518
7.5395
7.5276
7.4494
7.4475
7.4370
5.6772
4.7896
3.9147
Ru
OC
CO
NH2
+
8
7
6
5
4
3
[ppm]

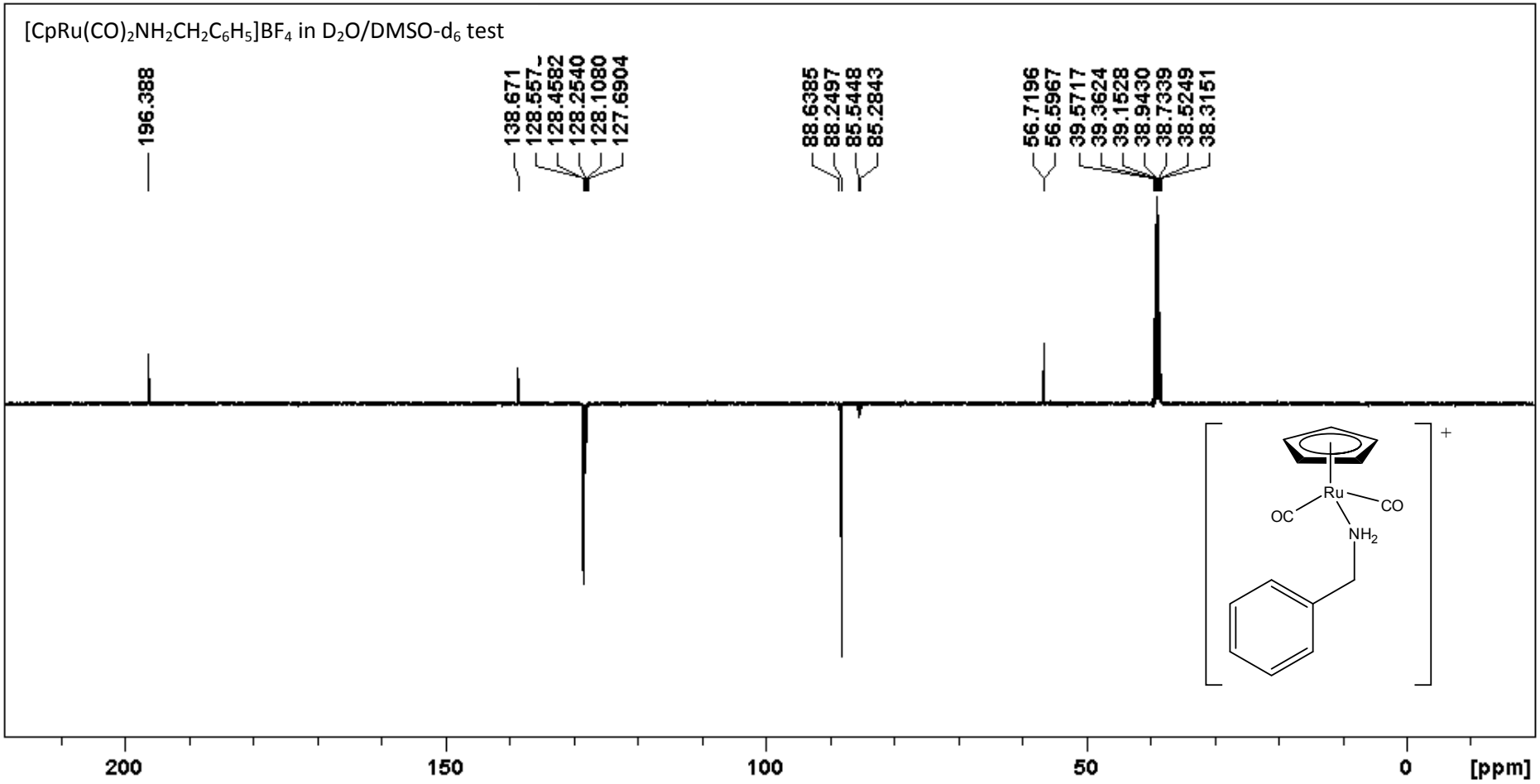

[CpRu(CO)2NH2CH2C6H5]BF4 in D2O at 50 °C
7.7858
7.7733
7.7617
7.6773
7.6667
5.9005
4.8001
4.1390
Ru
CO
OC
NH2
+
8
7
6
5
4
[ppm]

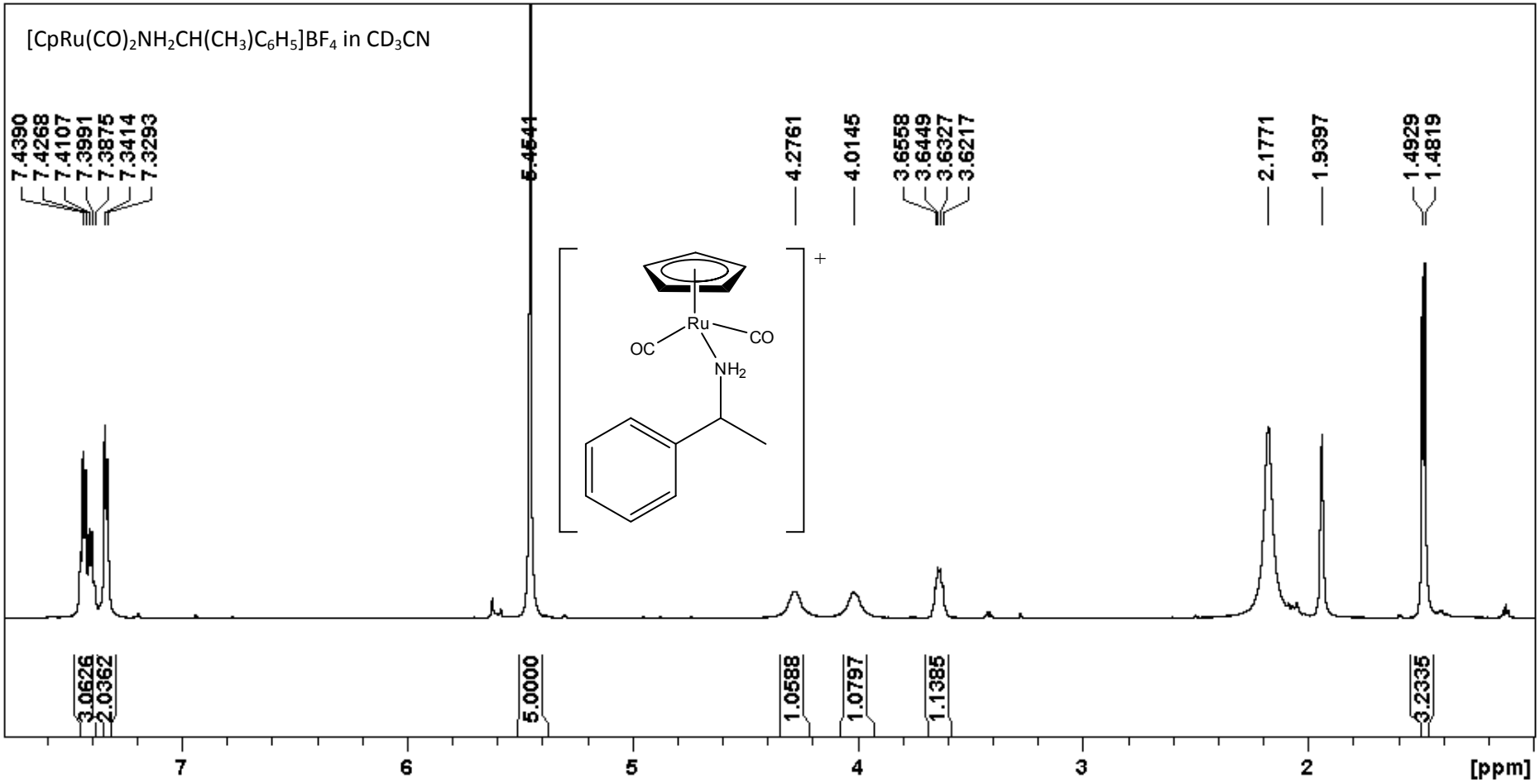

[CpRu(CO)2NH2CH2C6H5]BF4 in D2O at 30 °C
Ru
OC
CO
NH2
F1 [ppm]
F2 [ppm]
40
60
80
100
120
140
8
7
6
5
4
3

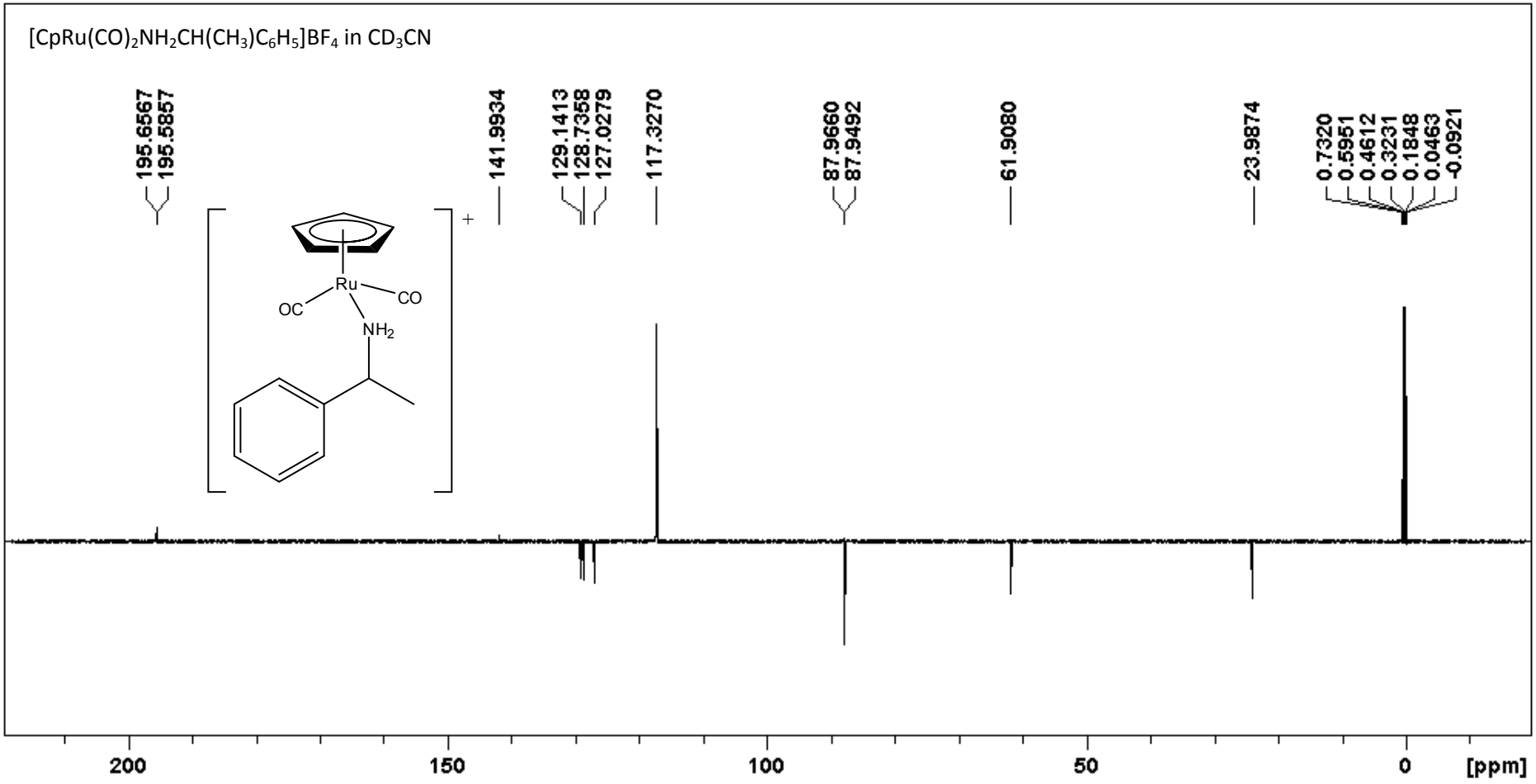

[CpRu(CO)2NH2CH2C6H5]BF4 in DMSO-d6
7.4176
7.3966
7.3832
7.3690
7.3654
7.3565
7.3478
5.7886
5.7774
5.3273
3.7122
3.6946
3.6769
3.3346
3.3111
2.5024
2.4979
2.4937
2.4892
Ru
OC
CO
NH2
5.0873
5.0000
1.8756
2.1389
8
7
6
5
4
3
[ppm]

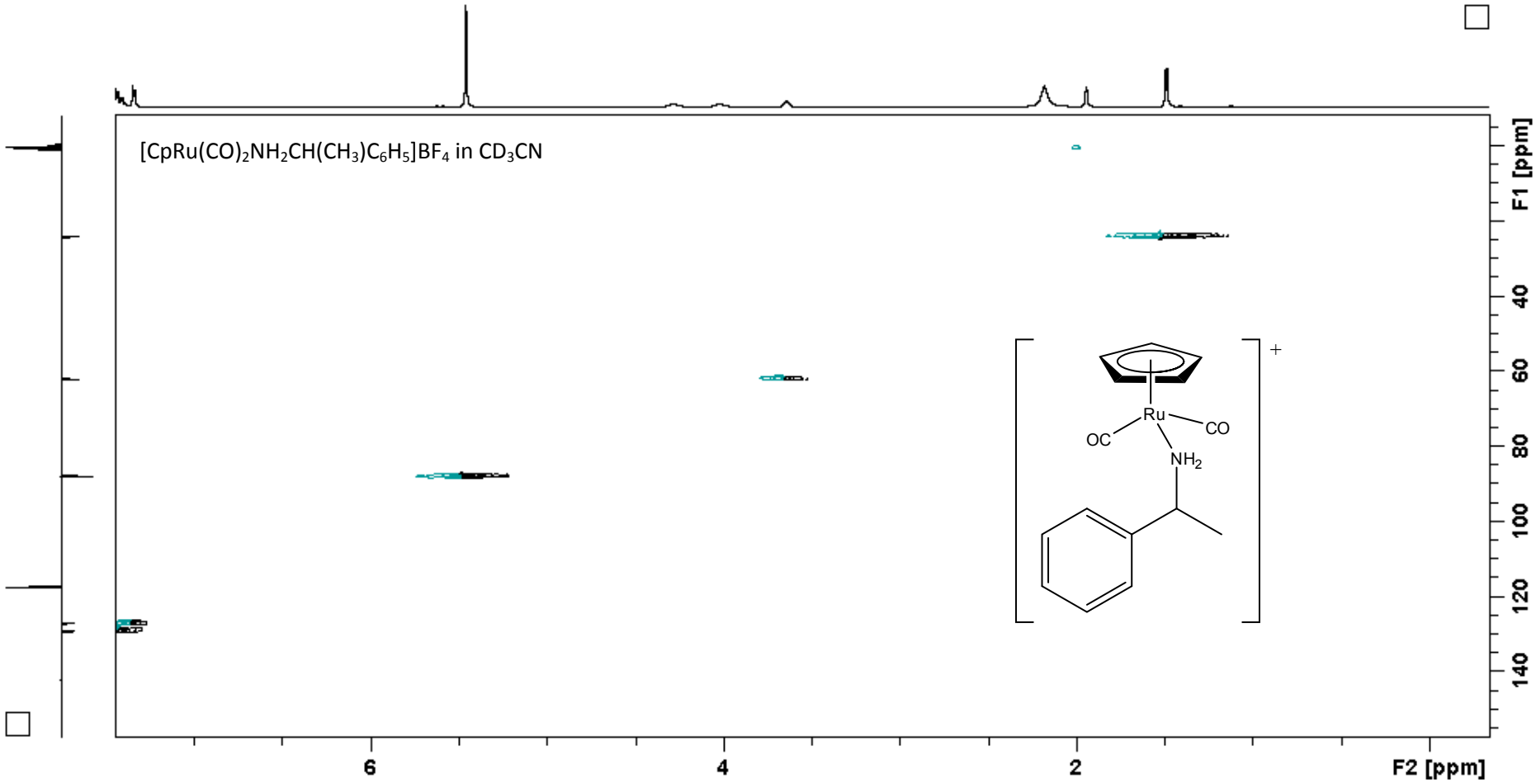

[CpRu(CO)2NH2CH2C6H5]BF4 in D2O/DMSO-d6 test
7.3659
7.3529
7.3399
5.6995
3.7770
3.6484
2.5033
2.4988
2.4943
Ru
OC
CO
NH2
+
8
7
6
5
4
3
[ppm]

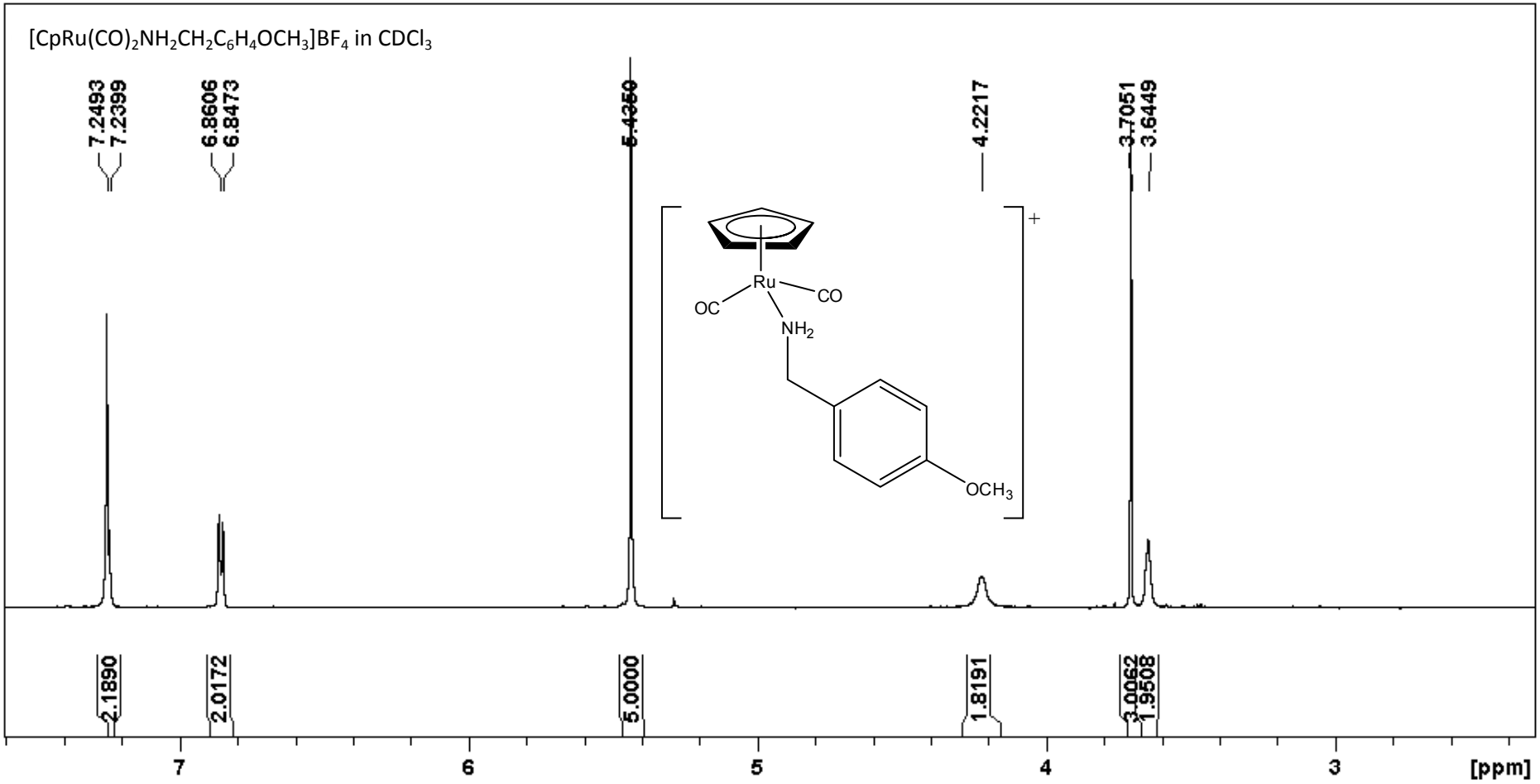

[CpRu(CO)2NH2CH2C6H5]BF4 in D2O/DMSO-d6 test
[CpRu(CO)2NH2CH2C6H5]BF4 in DMSO-d6
Ru
OC
CO
NH2
+
8
7
6
5
4
3
[ppm]

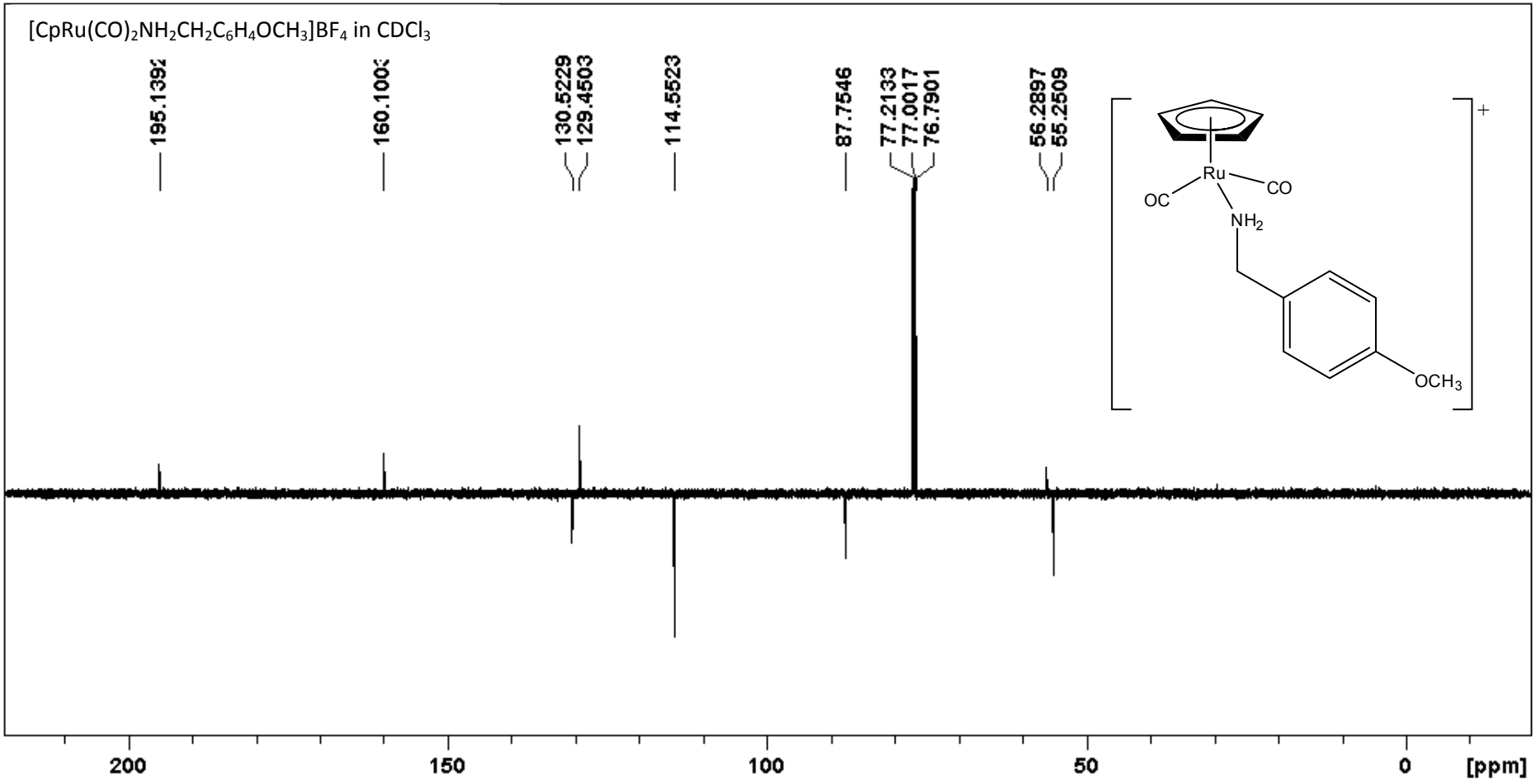

[CpRu(CO)2NH2CH2C6H5]BF4 in D2O/DMSO-d6 test
196.388
138.671
128.557
128.4582
128.2540
128.1080
127.6904
88.6385
88.2497
85.5448
85.2843
56.7196
56.5967
39.5717
39.3624
39.1528
38.9430
38.7339
38.5249
38.3151
Ru
CO
OC
NH2
+
200
150
100
50
0
[ppm]

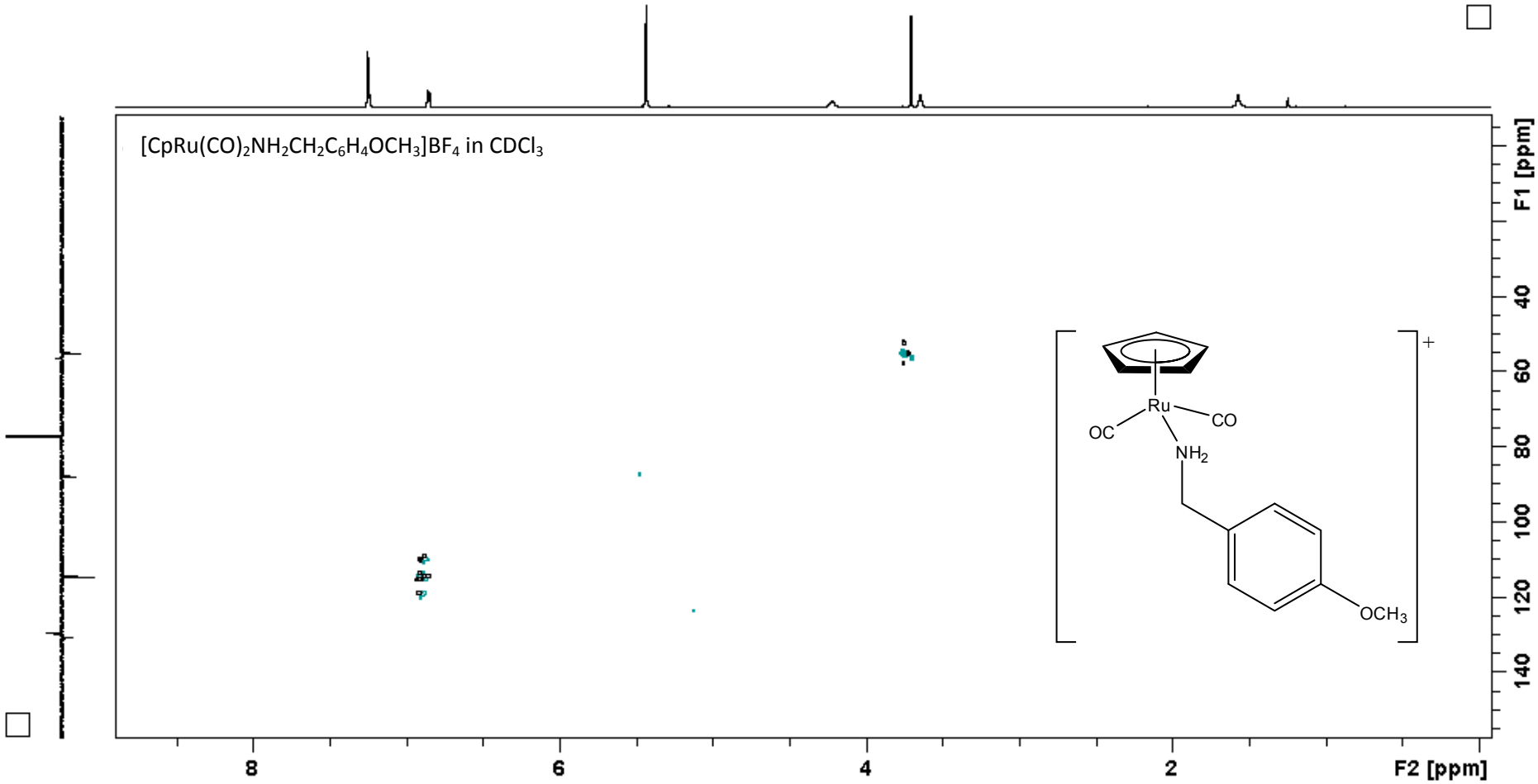

[CpRu(CO)2NH2CH(CH3)C6H5]BF4 in CD3CN
7.4390
7.4268
7.4107
7.3991
7.3875
7.3414
7.3293
5.4544
4.2761
4.0145
3.6558
3.6449
3.6327
3.6217
2.1771
1.9397
1.4929
1.4819
Ru
OC
CO
NH2
+
3.0626
2.0362
5.0000
1.0588
1.0797
1.1385
3.2335
7
6
5
4
3
2
[ppm]

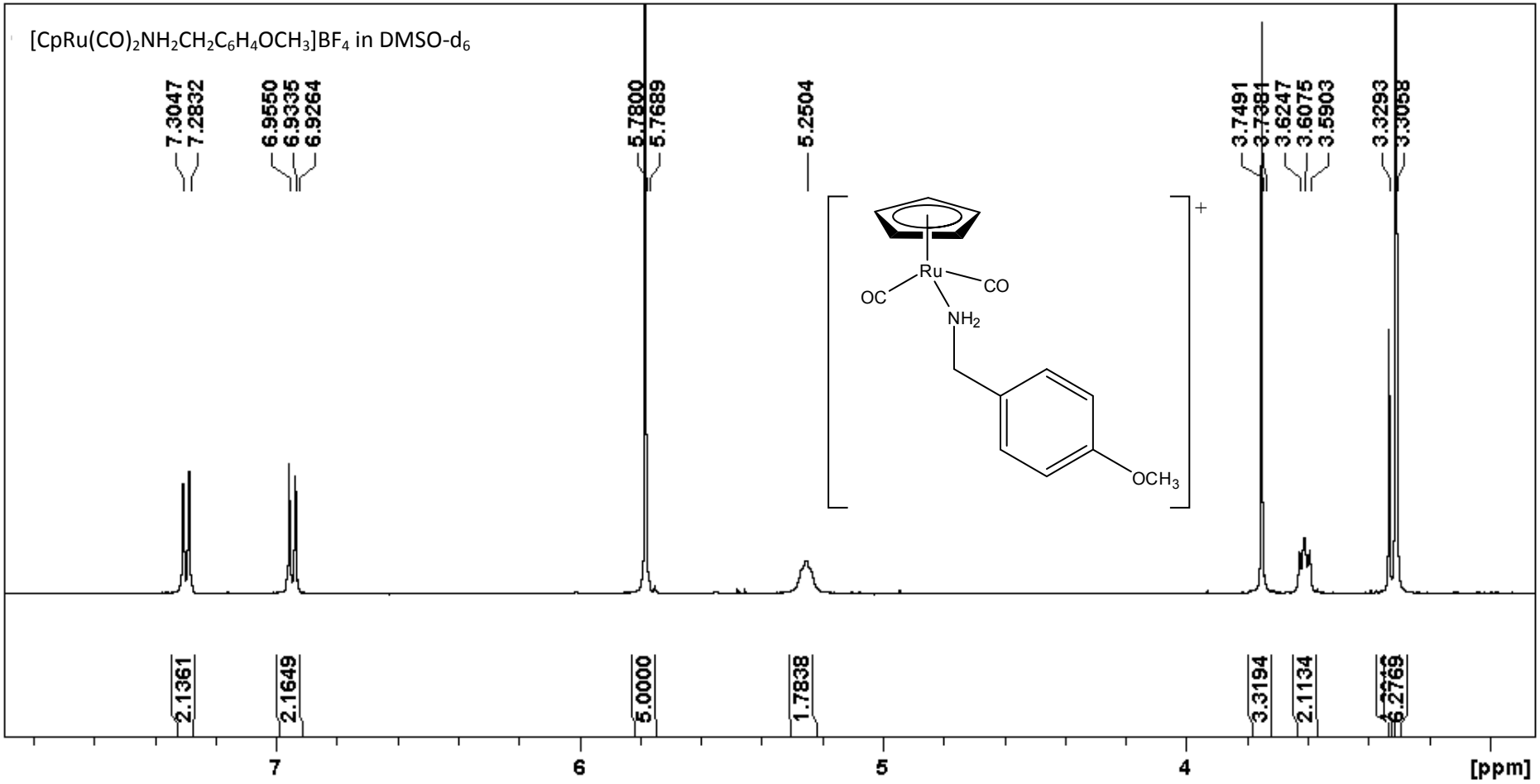

[CpRu(CO)2NH2CH(CH3)C6H5]BF4 in CD3CN
195.6567
195.5857
141.9934
129.1413
128.7358
127.0279
117.3270
87.9660
87.9492
61.9080
23.9874
0.7320
0.5951
0.4612
0.3231
0.1848
0.0463
-0.0921
Ru
OC
CO
NH2
+
200
150
100
50
0
[ppm]

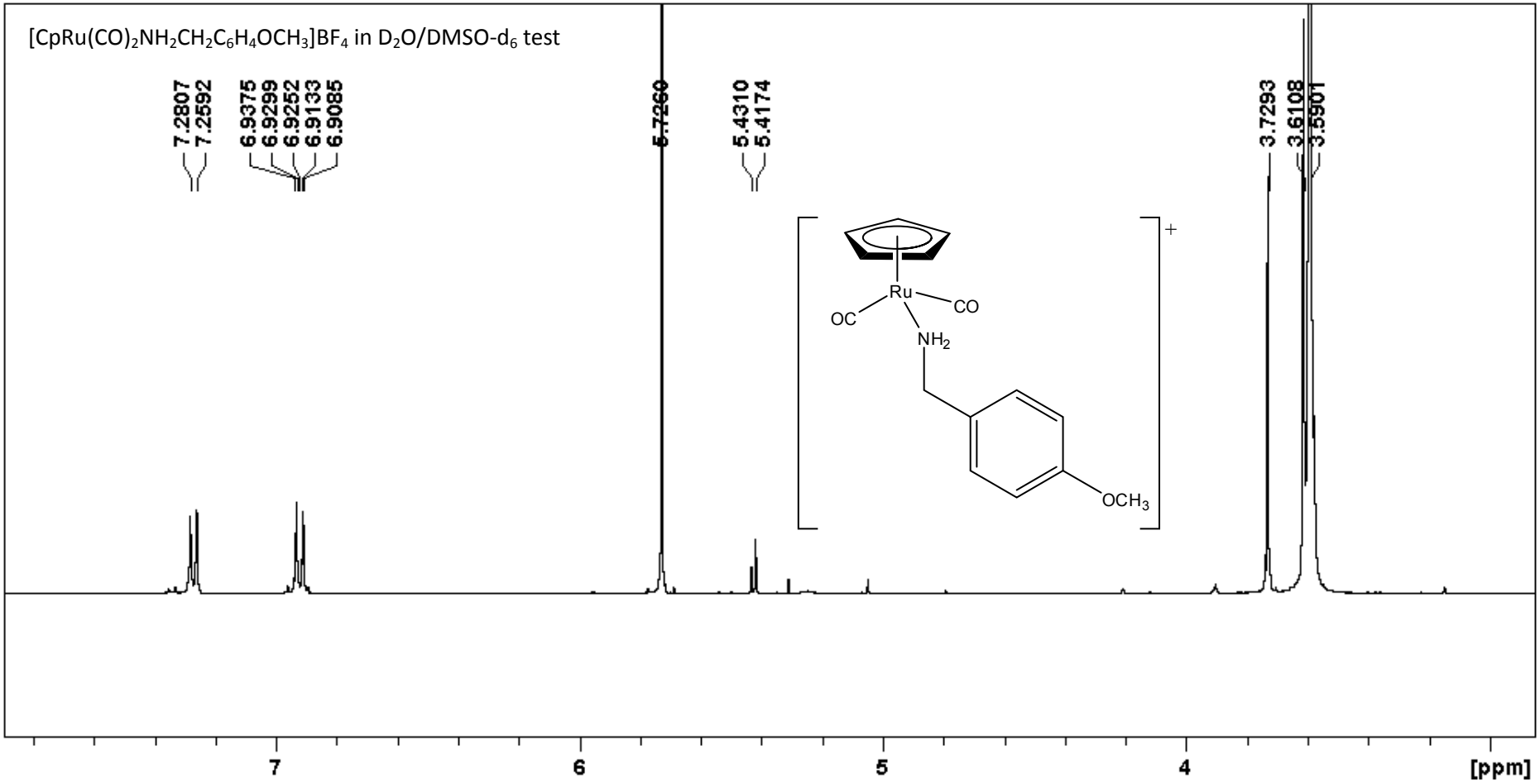

[CpRu(CO)2NH2CH(CH3)C6H5]BF4 in CD3CN
Ru
CO
OC
NH2
+
F1 [ppm]
40
60
80
100
120
140
6
4
2
F2 [ppm]

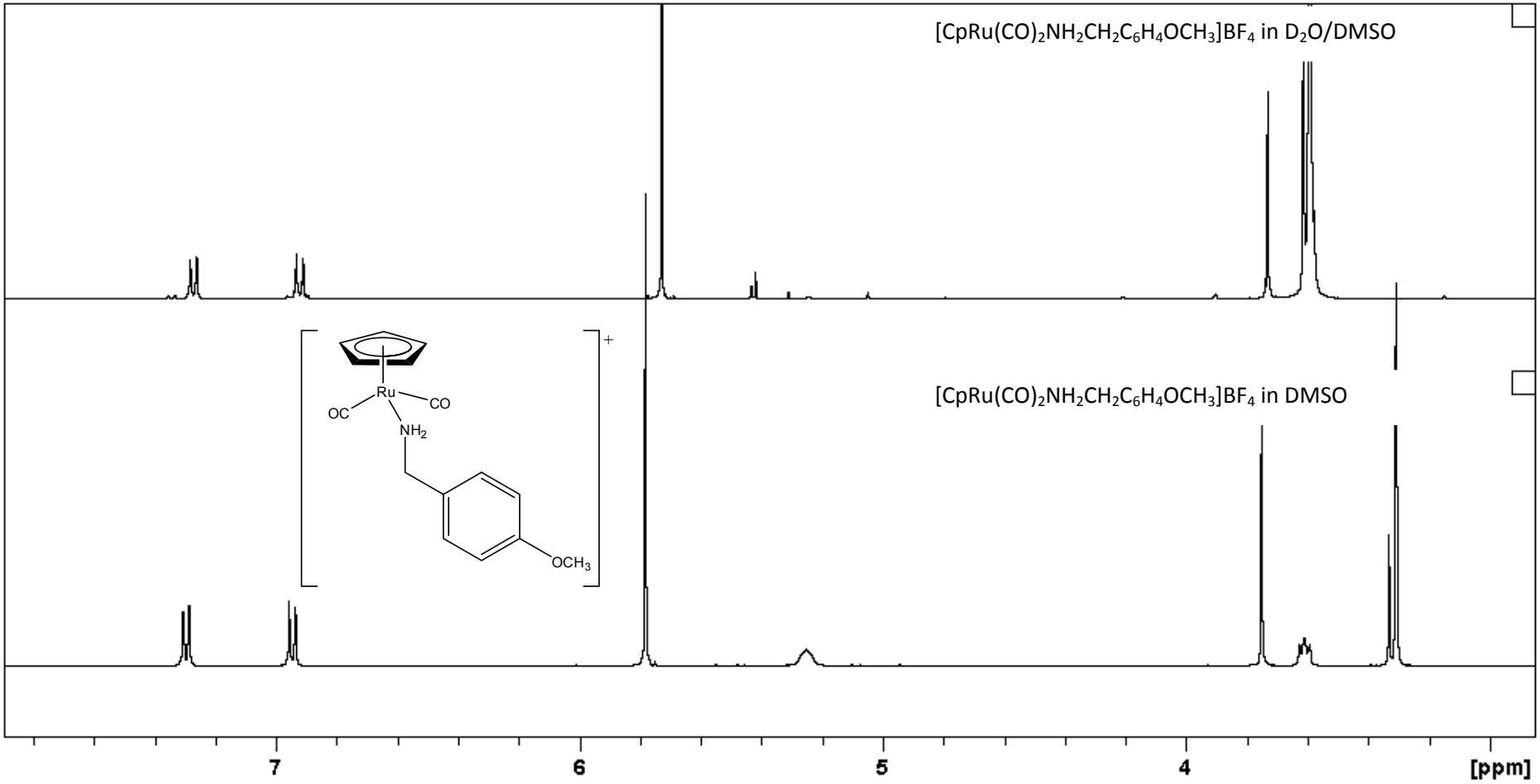

[CpRu(CO)2NH2CH2C6H4OCH3]BF4 in CDCl3
7.2493
7.2399
6.8606
6.8473
5.4350
4.2217
3.7051
3.6449
Ru
CO
OC
NH2
OCH3
+
2.1890
2.0172
5.0000
1.8191
3.0062
1.9508
7
6
5
4
3
[ppm]

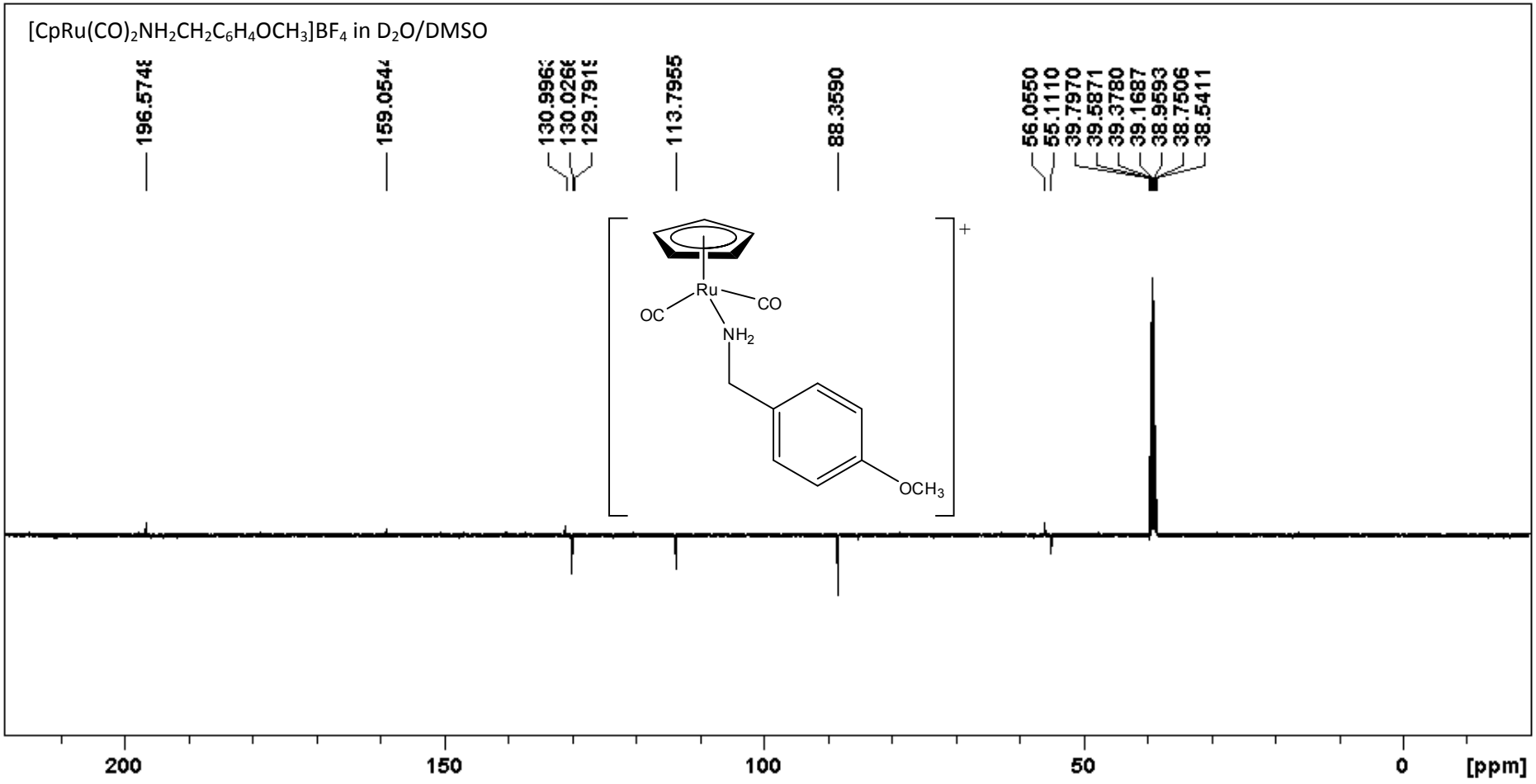

[CpRu(CO)2NH2CH2C6H4OCH3]BF4 in CDCl3
195.139
160.100
130.5229
129.4503
114.5523
87.7546
77.2133
77.0017
76.7901
56.2897
55.2509
Ru
CO
OC
NH2
OCH3
+
200
150
100
50
0
[ppm]

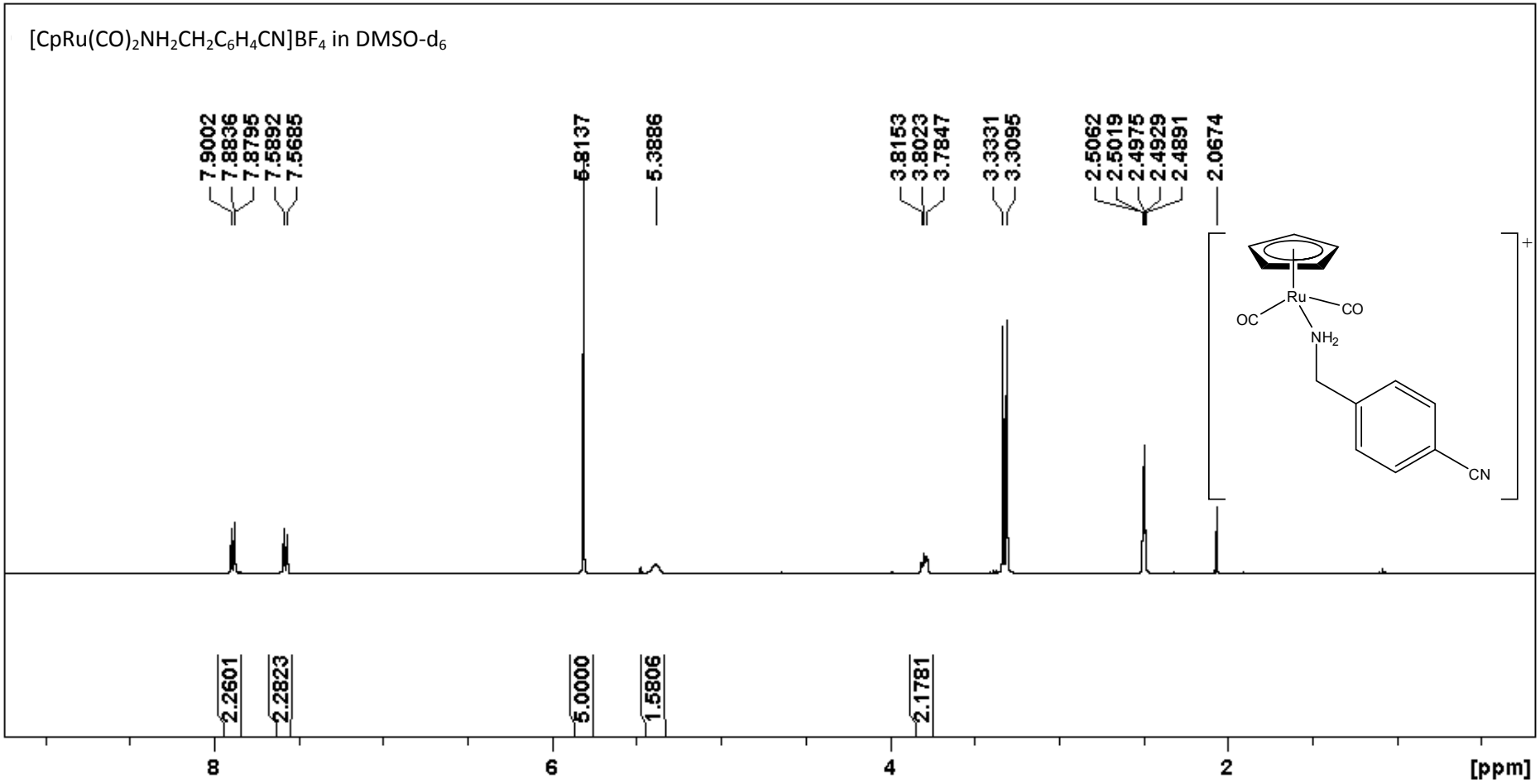

[CpRu(CO)2NH2CH2C6H4OCH3]BF4 in CDCl3
Ru
CO
OC
NH2
OCH3
+
F1 [ppm]
40
60
80
100
120
140
8
6
4
2
F2 [ppm]

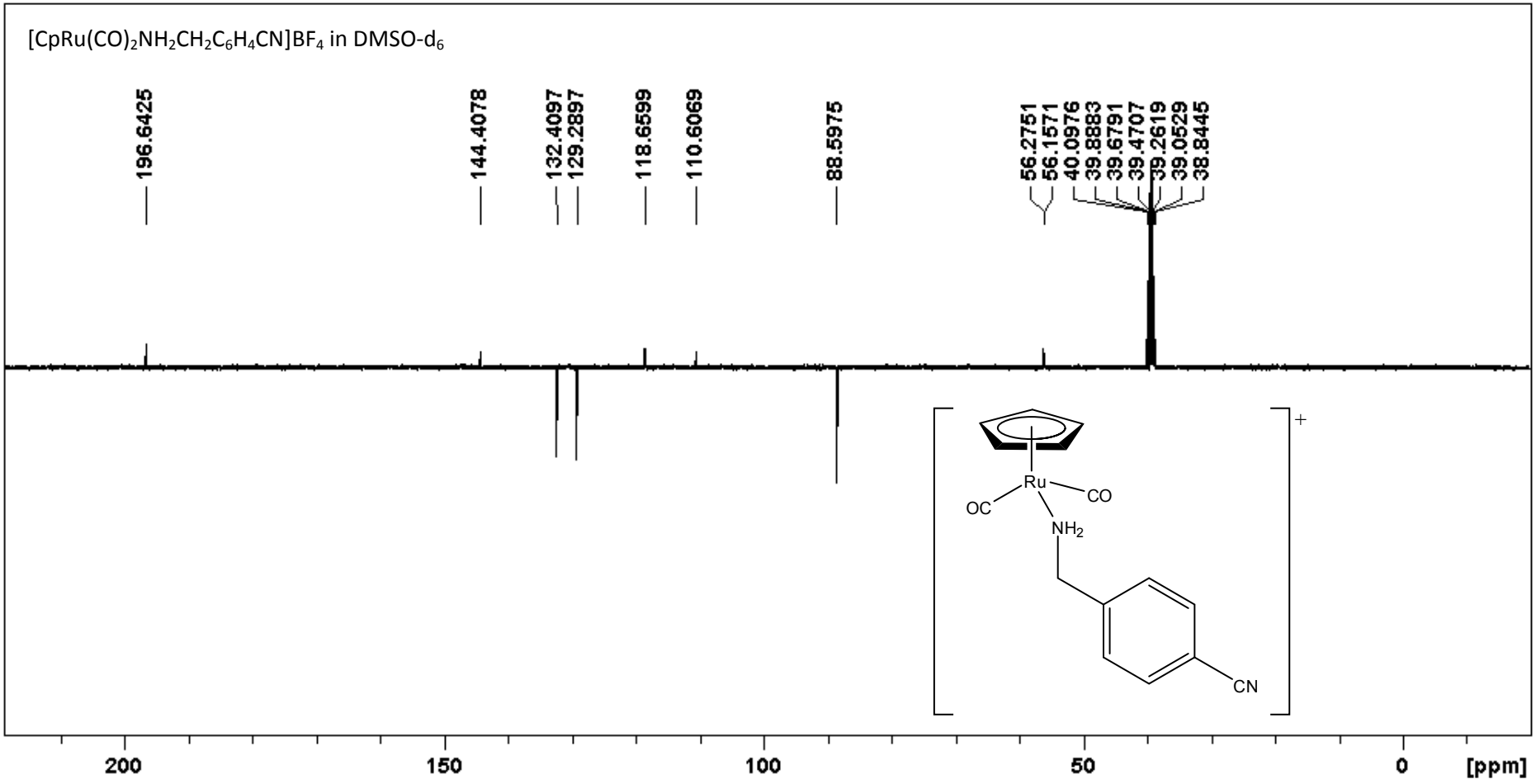

[CpRu(CO)2NH2CH2C6H4OCH3]BF4 in DMSO-d6
7.3047
7.2832
6.9550
6.9335
6.9264
5.7800
5.7689
5.2504
3.7491
3.7381
3.6247
3.6075
3.5903
3.3293
3.3058
Ru
CO
OC
NH2
OCH3
+
2.1361
2.1649
5.0000
1.7838
3.3194
2.1134
6.2769
7
6
5
4
[ppm]

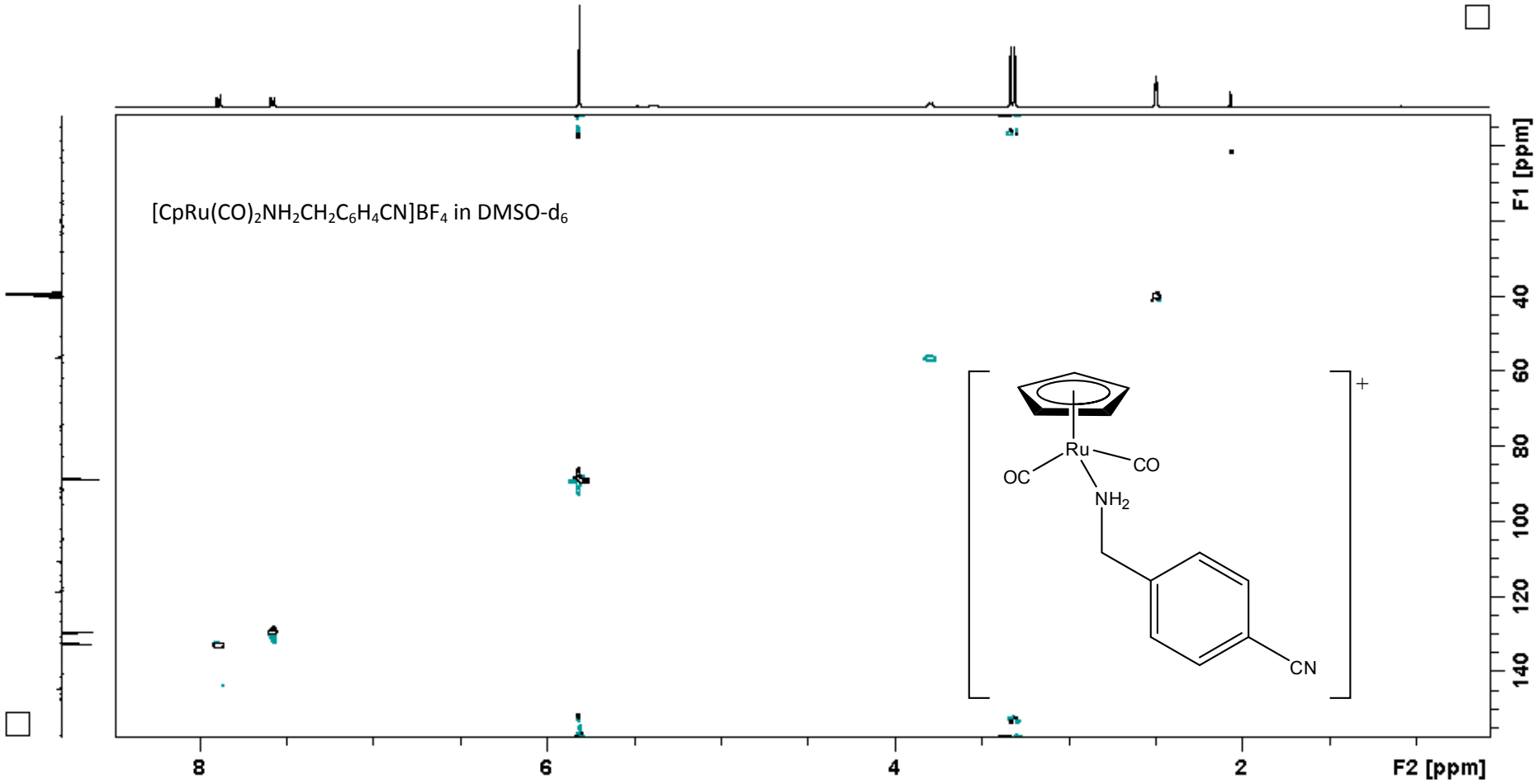

[CpRu(CO)2NH2CH2C6H4OCH3]BF4 in D2O/DMSO-d6 test
7.2807
7.2592
6.9375
6.9299
6.9252
6.9133
6.9085
5.7260
5.4310
5.4174
3.7293
3.6108
3.5901
Ru
CO
OC
NH2
OCH3
+
7
6
5
4
[ppm]


[CpRu(CO)2NH2CH2C6H4OCH3]BF4 in D2O/DMSO
[CpRu(CO)2NH2CH2C6H4OCH3]BF4 in DMSO
Ru
CO
OC
NH2
OCH3
+
7
6
5
4
[ppm]


[CpRu(CO)2NH2CH2C6H4OCH3]BF4 in D2O/DMSO
196.5748
159.0544
130.9963
130.0266
129.7915
113.7955
88.3590
56.0550
55.1110
39.7970
39.5871
39.3780
39.1687
38.9593
38.7506
38.5411
Ru
CO
OC
NH2
OCH3
+
200
150
100
50
0
[ppm]


[CpRu(CO)2NH2CH2C6H4CN]BF4 in DMSO-d6
7.9002
7.8836
7.8795
7.5892
7.5685
5.8137
5.3886
3.8153
3.8023
3.7847
3.3331
3.3095
2.5062
2.5019
2.4975
2.4929
2.4891
2.0674
Ru
CO
OC
NH2
CN
+
2.2601
2.2823
5.0000
1.5806
2.1781
8
6
4
2
[ppm]


[CpRu(CO)2NH2CH2C6H4CN]BF4 in DMSO-d6
196.6425
144.4078
132.4097
129.2897
118.6599
110.6069
88.5975
56.2751
56.1571
40.0976
39.8883
39.6791
39.4707
39.2619
39.0529
38.8445
Ru
CO
OC
NH2
CN
+
200
150
100
50
0
[ppm]


[CpRu(CO)2NH2CH2C6H4CN]BF4 in DMSO-d6
F1 [ppm]
F2 [ppm]
8
6
4
2
40
60
80
100
120
140
Ru
OC
CO
NH2
CN
+

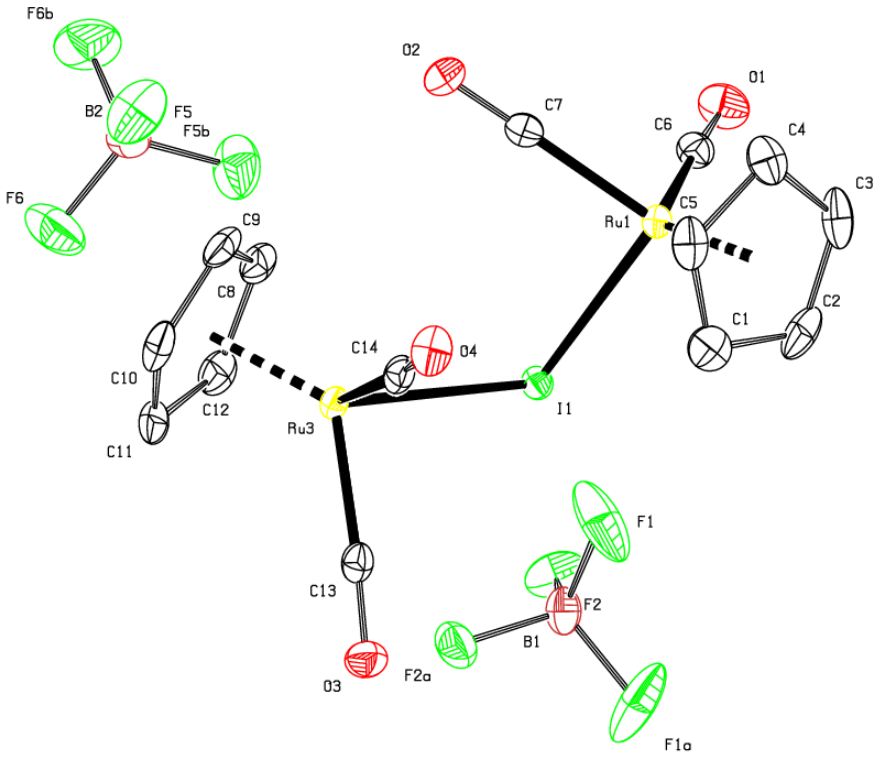
# APPENDIX B:

## CRYSTAL STRUCTURE TABLES PERTAINING TO CHAPTERS 2 - 6

# Table of Contents

# STRUCTURE TABLES PERTAINING TO CHAPTER 2

## POLYMORPH I – $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2I\}BF_4$




**ORTEP diagram**

**Table B1:** Crystal data and structure refinement for Polymorph I – $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2I\}BF_4$

| | | |
|---|---|---|
| Empirical formula | C14 H10 B F4 I O4 Ru2 | |
| Formula weight | 658.07 | |
| Temperature | 446(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2/c | |
| Unit cell dimensions | a = 12.0982(5) Å | α= 90°. |
| | b = 9.7923(4) Å | β= 102.9880(10)°. |
| | c = 15.5321(6) Å | γ = 90°. |
| Volume | 1793.00(13) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 2.438 $Mg/m^3$ | |
| Absorption coefficient | 3.462 $mm^{-1}$ | |
| F(000) | 1232 | |
| Crystal size | 0.43 x 0.34 x 0.16 $mm^3$ | |
| Theta range for data collection | 1.73 to 28.45°. | |
| Index ranges | -16<=h<=15, -13<=k<=11, -20<=l<=20 | |
| Reflections collected | 46542 | |
| Independent reflections | 4492 [R(int) = 0.0247] | |
| Completeness to theta = 28.45° | 99.2 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.6858 and 0.4069 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4492 / 0 / 236 | |
| Goodness-of-fit on $F^2$ | 1.201 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0141, wR2 = 0.0378 | |
| R indices (all data) | R1 = 0.0149, wR2 = 0.0385 | |
| Largest diff. peak and hole | 0.408 and -0.837 $e.Å^{-3}$ | |

**Table B2:** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) {[$\eta^5$-$C_5H_5Ru(CO)_2]_2I$}$BF_4$ U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 2034(2) | 4434(2) | 9976(1) | 27(1) |
| C(2) | 1928(2) | 4046(2) | 10849(2) | 29(1) |
| C(3) | 3014(2) | 3657(2) | 11328(1) | 28(1) |
| C(4) | 3804(2) | 3851(2) | 10783(1) | 25(1) |
| C(5) | 3176(2) | 4299(2) | 9939(1) | 24(1) |
| C(6) | 3428(2) | 6406(2) | 12178(1) | 20(1) |
| C(7) | 4111(2) | 7101(2) | 10681(1) | 19(1) |
| C(8) | 2854(2) | 10569(2) | 9953(1) | 23(1) |
| C(9) | 3268(2) | 10195(2) | 9211(1) | 24(1) |
| C(10) | 2448(2) | 10582(2) | 8435(1) | 27(1) |
| C(11) | 1533(2) | 11233(2) | 8710(1) | 26(1) |
| C(12) | 1766(2) | 11201(2) | 9649(1) | 24(1) |
| C(13) | 98(2) | 8717(2) | 8619(1) | 19(1) |
| C(14) | 2130(2) | 7473(2) | 8640(1) | 18(1) |
| O(1) | 3664(1) | 6662(2) | 12908(1) | 30(1) |
| O(2) | 4742(1) | 7807(1) | 10463(1) | 26(1) |
| O(3) | -838(1) | 8576(2) | 8297(1) | 26(1) |
| O(4) | 2494(1) | 6578(1) | 8332(1) | 25(1) |
| Ru(1) | 3054(1) | 5858(1) | 10975(1) | 13(1) |
| Ru(3) | 1639(1) | 9071(1) | 9147(1) | 14(1) |
| I(1) | 1405(1) | 7749(1) | 10619(1) | 15(1) |
| B(2) | 5000 | 9224(3) | 7500 | 24(1) |
| F(5) | 4529(1) | 8393(2) | 8047(1) | 45(1) |
| F(6) | 5834(1) | 10037(2) | 8001(1) | 50(1) |
| B(1) | 10000 | 5317(3) | 2500 | 23(1) |
| F(1) | 9044(2) | 6115(2) | 2447(1) | 58(1) |
| F(2) | 9857(1) | 4493(1) | 1754(1) | 34(1) |

**Table B3:** Bond lengths [Å] and angles [°] for $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2I\}BF_4$

| | |
|---|---|
| C(1)-C(5) | 1.401(3) |
| C(1)-C(2) | 1.442(3) |
| C(1)-Ru(1) | 2.2395(18) |
| C(1)-H(1) | 0.9800 |
| C(2)-C(3) | 1.408(3) |
| C(2)-Ru(1) | 2.2181(18) |
| C(2)-H(2) | 0.9800 |
| C(3)-C(4) | 1.424(3) |
| C(3)-Ru(1) | 2.2271(19) |
| C(3)-H(3) | 0.9800 |
| C(4)-C(5) | 1.429(3) |
| C(4)-Ru(1) | 2.2132(18) |
| C(4)-H(4) | 0.9800 |
| C(5)-Ru(1) | 2.2472(17) |
| C(5)-H(5) | 0.9800 |
| C(6)-O(1) | 1.132(2) |
| C(6)-Ru(1) | 1.8989(18) |
| C(7)-O(2) | 1.136(2) |
| C(7)-Ru(1) | 1.8943(18) |
| C(8)-C(9) | 1.405(3) |
| C(8)-C(12) | 1.435(3) |
| C(8)-Ru(3) | 2.2482(18) |
| C(8)-H(8) | 0.9800 |
| C(9)-C(10) | 1.429(3) |
| C(9)-Ru(3) | 2.2400(18) |
| C(9)-H(9) | 0.9800 |
| C(10)-C(11) | 1.424(3) |
| C(10)-Ru(3) | 2.2042(18) |
| C(10)-H(10) | 0.9800 |
| C(11)-C(12) | 1.423(3) |
| C(11)-Ru(3) | 2.2180(18) |
| C(11)-H(11) | 0.9800 |
| C(12)-Ru(3) | 2.2198(18) |
| C(12)-H(12) | 0.9800 |
| C(13)-O(3) | 1.139(2) |
| C(13)-Ru(3) | 1.8922(18) |

| | |
|---|---|
| C(14)-O(4) | 1.134(2) |
| C(14)-Ru(3) | 1.9058(18) |
| Ru(1)-I(1) | 2.68658(18) |
| Ru(3)-I(1) | 2.69707(18) |
| B(2)-F(6) | 1.380(2) |
| B(2)-F(6)#1 | 1.380(2) |
| B(2)-F(5)#1 | 1.388(2) |
| B(2)-F(5) | 1.388(2) |
| B(1)-F(1)#2 | 1.382(2) |
| B(1)-F(1) | 1.382(2) |
| B(1)-F(2) | 1.390(2) |
| B(1)-F(2)#2 | 1.390(2) |

| | |
|---|---|
| C(5)-C(1)-C(2) | 108.07(18) |
| C(5)-C(1)-Ru(1) | 72.11(11) |
| C(2)-C(1)-Ru(1) | 70.32(11) |
| C(5)-C(1)-H(1) | 125.9 |
| C(2)-C(1)-H(1) | 125.9 |
| Ru(1)-C(1)-H(1) | 125.9 |
| C(3)-C(2)-C(1) | 107.37(17) |
| C(3)-C(2)-Ru(1) | 71.87(11) |
| C(1)-C(2)-Ru(1) | 71.92(11) |
| C(3)-C(2)-H(2) | 126.2 |
| C(1)-C(2)-H(2) | 126.2 |
| Ru(1)-C(2)-H(2) | 126.2 |
| C(2)-C(3)-C(4) | 108.72(17) |
| C(2)-C(3)-Ru(1) | 71.18(11) |
| C(4)-C(3)-Ru(1) | 70.76(11) |
| C(2)-C(3)-H(3) | 125.6 |
| C(4)-C(3)-H(3) | 125.6 |
| Ru(1)-C(3)-H(3) | 125.6 |
| C(3)-C(4)-C(5) | 107.25(18) |
| C(3)-C(4)-Ru(1) | 71.82(11) |
| C(5)-C(4)-Ru(1) | 72.61(10) |
| C(3)-C(4)-H(4) | 126.2 |
| C(5)-C(4)-H(4) | 126.2 |
| Ru(1)-C(4)-H(4) | 126.2 |
| C(1)-C(5)-C(4) | 108.51(17) |

| | |
|---|---|
| C(1)-C(5)-Ru(1) | 71.51(10) |
| C(4)-C(5)-Ru(1) | 70.02(10) |
| C(1)-C(5)-H(5) | 125.7 |
| C(4)-C(5)-H(5) | 125.7 |
| Ru(1)-C(5)-H(5) | 125.7 |
| O(1)-C(6)-Ru(1) | 176.35(17) |
| O(2)-C(7)-Ru(1) | 176.25(16) |
| C(9)-C(8)-C(12) | 108.23(17) |
| C(9)-C(8)-Ru(3) | 71.45(11) |
| C(12)-C(8)-Ru(3) | 70.20(10) |
| C(9)-C(8)-H(8) | 125.9 |
| C(12)-C(8)-H(8) | 125.9 |
| Ru(3)-C(8)-H(8) | 125.9 |
| C(8)-C(9)-C(10) | 108.34(17) |
| C(8)-C(9)-Ru(3) | 72.08(10) |
| C(10)-C(9)-Ru(3) | 69.89(10) |
| C(8)-C(9)-H(9) | 125.8 |
| C(10)-C(9)-H(9) | 125.8 |
| Ru(3)-C(9)-H(9) | 125.8 |
| C(11)-C(10)-C(9) | 107.75(17) |
| C(11)-C(10)-Ru(3) | 71.75(10) |
| C(9)-C(10)-Ru(3) | 72.61(10) |
| C(11)-C(10)-H(10) | 126.0 |
| C(9)-C(10)-H(10) | 126.0 |
| Ru(3)-C(10)-H(10) | 126.0 |
| C(12)-C(11)-C(10) | 108.05(17) |
| C(12)-C(11)-Ru(3) | 71.37(10) |
| C(10)-C(11)-Ru(3) | 70.69(11) |
| C(12)-C(11)-H(11) | 125.9 |
| C(10)-C(11)-H(11) | 125.9 |
| Ru(3)-C(11)-H(11) | 125.9 |
| C(11)-C(12)-C(8) | 107.58(17) |
| C(11)-C(12)-Ru(3) | 71.23(10) |
| C(8)-C(12)-Ru(3) | 72.34(11) |
| C(11)-C(12)-H(12) | 126.1 |
| C(8)-C(12)-H(12) | 126.1 |
| Ru(3)-C(12)-H(12) | 126.1 |
| O(3)-C(13)-Ru(3) | 176.41(16) |

| | |
|---|---|
| O(4)-C(14)-Ru(3) | 174.66(15) |
| C(7)-Ru(1)-C(6) | 91.80(8) |
| C(7)-Ru(1)-C(4) | 102.65(8) |
| C(6)-Ru(1)-C(4) | 111.67(7) |
| C(7)-Ru(1)-C(2) | 157.98(8) |
| C(6)-Ru(1)-C(2) | 108.57(8) |
| C(4)-Ru(1)-C(2) | 62.60(8) |
| C(7)-Ru(1)-C(3) | 137.26(8) |
| C(6)-Ru(1)-C(3) | 92.56(7) |
| C(4)-Ru(1)-C(3) | 37.41(7) |
| C(2)-Ru(1)-C(3) | 36.95(8) |
| C(7)-Ru(1)-C(1) | 121.97(8) |
| C(6)-Ru(1)-C(1) | 146.15(8) |
| C(4)-Ru(1)-C(1) | 62.11(8) |
| C(2)-Ru(1)-C(1) | 37.76(8) |
| C(3)-Ru(1)-C(1) | 61.90(8) |
| C(7)-Ru(1)-C(5) | 96.17(7) |
| C(6)-Ru(1)-C(5) | 149.03(7) |
| C(4)-Ru(1)-C(5) | 37.37(7) |
| C(2)-Ru(1)-C(5) | 62.04(7) |
| C(3)-Ru(1)-C(5) | 61.79(7) |
| C(1)-Ru(1)-C(5) | 36.39(8) |
| C(7)-Ru(1)-I(1) | 91.01(5) |
| C(6)-Ru(1)-I(1) | 90.56(5) |
| C(4)-Ru(1)-I(1) | 153.17(6) |
| C(2)-Ru(1)-I(1) | 96.92(6) |
| C(3)-Ru(1)-I(1) | 131.42(6) |
| C(1)-Ru(1)-I(1) | 91.07(5) |
| C(5)-Ru(1)-I(1) | 119.07(5) |
| C(13)-Ru(3)-C(14) | 92.24(8) |
| C(13)-Ru(3)-C(10) | 114.29(8) |
| C(14)-Ru(3)-C(10) | 97.42(7) |
| C(13)-Ru(3)-C(11) | 93.38(7) |
| C(14)-Ru(3)-C(11) | 131.24(7) |
| C(10)-Ru(3)-C(11) | 37.56(8) |
| C(13)-Ru(3)-C(12) | 107.94(7) |
| C(14)-Ru(3)-C(12) | 155.96(7) |
| C(10)-Ru(3)-C(12) | 62.75(7) |

| | |
|---|---|
| C(11)-Ru(3)-C(12) | 37.40(7) |
| C(13)-Ru(3)-C(9) | 151.73(7) |
| C(14)-Ru(3)-C(9) | 93.94(7) |
| C(10)-Ru(3)-C(9) | 37.51(8) |
| C(11)-Ru(3)-C(9) | 62.25(7) |
| C(12)-Ru(3)-C(9) | 62.11(7) |
| C(13)-Ru(3)-C(8) | 144.89(8) |
| C(14)-Ru(3)-C(8) | 122.70(8) |
| C(10)-Ru(3)-C(8) | 62.13(7) |
| C(11)-Ru(3)-C(8) | 62.16(7) |
| C(12)-Ru(3)-C(8) | 37.46(7) |
| C(9)-Ru(3)-C(8) | 36.48(7) |
| C(13)-Ru(3)-I(1) | 89.91(5) |
| C(14)-Ru(3)-I(1) | 93.31(5) |
| C(10)-Ru(3)-I(1) | 152.95(5) |
| C(11)-Ru(3)-I(1) | 135.05(5) |
| C(12)-Ru(3)-I(1) | 99.51(5) |
| C(9)-Ru(3)-I(1) | 117.20(5) |
| C(8)-Ru(3)-I(1) | 91.22(5) |
| Ru(1)-I(1)-Ru(3) | 106.913(5) |
| F(6)-B(2)-F(6)#1 | 109.5(3) |
| F(6)-B(2)-F(5)#1 | 109.55(9) |
| F(6)#1-B(2)-F(5)#1 | 109.99(10) |
| F(6)-B(2)-F(5) | 109.99(10) |
| F(6)#1-B(2)-F(5) | 109.55(9) |
| F(5)#1-B(2)-F(5) | 108.3(3) |
| F(1)#2-B(1)-F(1) | 111.2(3) |
| F(1)#2-B(1)-F(2) | 108.87(8) |
| F(1)-B(1)-F(2) | 109.42(9) |
| F(1)#2-B(1)-F(2)#2 | 109.42(9) |
| F(1)-B(1)-F(2)#2 | 108.87(8) |
| F(2)-B(1)-F(2)#2 | 109.0(2) |

---

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2  #2 -x+2,y,-z+1/2

**Table B4:** Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2I\}BF_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 33(1) | 15(1) | 29(1) | -8(1) | -1(1) | -3(1) |
| C(2) | 34(1) | 14(1) | 44(1) | -8(1) | 21(1) | -9(1) |
| C(3) | 53(1) | 13(1) | 22(1) | 2(1) | 17(1) | 3(1) |
| C(4) | 33(1) | 17(1) | 26(1) | -1(1) | 10(1) | 8(1) |
| C(5) | 41(1) | 15(1) | 19(1) | -3(1) | 13(1) | 1(1) |
| C(6) | 18(1) | 19(1) | 22(1) | 0(1) | 4(1) | 2(1) |
| C(7) | 16(1) | 20(1) | 19(1) | 0(1) | 3(1) | 2(1) |
| C(8) | 26(1) | 17(1) | 26(1) | -2(1) | 2(1) | -9(1) |
| C(9) | 21(1) | 18(1) | 36(1) | -2(1) | 10(1) | -8(1) |
| C(10) | 36(1) | 21(1) | 26(1) | 2(1) | 12(1) | -12(1) |
| C(11) | 29(1) | 14(1) | 32(1) | 7(1) | 2(1) | -5(1) |
| C(12) | 27(1) | 14(1) | 31(1) | -4(1) | 9(1) | -4(1) |
| C(13) | 24(1) | 17(1) | 15(1) | 1(1) | 6(1) | -3(1) |
| C(14) | 21(1) | 19(1) | 16(1) | 2(1) | 6(1) | -5(1) |
| O(1) | 32(1) | 38(1) | 17(1) | -4(1) | 2(1) | 1(1) |
| O(2) | 18(1) | 29(1) | 32(1) | 5(1) | 8(1) | -4(1) |
| O(3) | 21(1) | 32(1) | 23(1) | 2(1) | 0(1) | -5(1) |
| O(4) | 33(1) | 22(1) | 25(1) | -3(1) | 15(1) | 0(1) |
| Ru(1) | 15(1) | 13(1) | 13(1) | 0(1) | 5(1) | 0(1) |
| Ru(3) | 15(1) | 12(1) | 14(1) | 0(1) | 4(1) | -2(1) |
| I(1) | 15(1) | 16(1) | 15(1) | 1(1) | 5(1) | 1(1) |
| B(2) | 22(1) | 32(2) | 20(1) | 0 | 4(1) | 0 |
| F(5) | 51(1) | 45(1) | 49(1) | 14(1) | 32(1) | 8(1) |
| F(6) | 44(1) | 62(1) | 36(1) | -13(1) | -6(1) | -13(1) |
| B(1) | 32(2) | 18(1) | 20(1) | 0 | 10(1) | 0 |
| F(1) | 87(1) | 52(1) | 44(1) | 21(1) | 34(1) | 50(1) |
| F(2) | 29(1) | 43(1) | 33(1) | -18(1) | 10(1) | -7(1) |

**Table B5:** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for {[$\eta^5$-$C_5H_5Ru(CO)_2]_2I$}.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 1410 | 4695 | 9483 | 32 |
| H(2) | 1220 | 3978 | 11053 | 34 |
| H(3) | 3192 | 3285 | 11929 | 34 |
| H(4) | 4612 | 3618 | 10937 | 30 |
| H(5) | 3487 | 4458 | 9417 | 29 |
| H(8) | 3253 | 10452 | 10571 | 28 |
| H(9) | 4007 | 9775 | 9223 | 29 |
| H(10) | 2537 | 10501 | 7825 | 32 |
| H(11) | 878 | 11669 | 8321 | 31 |
| H(12) | 1300 | 11611 | 10022 | 28 |

**Table B6:** Torsion angles [°] for {[$\eta^5$-$C_5H_5Ru(CO)_2]_2I$}.

| | |
|---|---|
| C(5)-C(1)-C(2)-C(3) | -1.0(2) |
| Ru(1)-C(1)-C(2)-C(3) | -63.58(13) |
| C(5)-C(1)-C(2)-Ru(1) | 62.62(13) |
| C(1)-C(2)-C(3)-C(4) | 2.5(2) |
| Ru(1)-C(2)-C(3)-C(4) | -61.12(14) |
| C(1)-C(2)-C(3)-Ru(1) | 63.61(12) |
| C(2)-C(3)-C(4)-C(5) | -3.1(2) |
| Ru(1)-C(3)-C(4)-C(5) | -64.44(13) |
| C(2)-C(3)-C(4)-Ru(1) | 61.38(13) |
| C(2)-C(1)-C(5)-C(4) | -0.9(2) |
| Ru(1)-C(1)-C(5)-C(4) | 60.54(13) |
| C(2)-C(1)-C(5)-Ru(1) | -61.47(12) |
| C(3)-C(4)-C(5)-C(1) | 2.4(2) |
| Ru(1)-C(4)-C(5)-C(1) | -61.47(13) |
| C(3)-C(4)-C(5)-Ru(1) | 63.92(13) |
| C(12)-C(8)-C(9)-C(10) | -0.1(2) |
| Ru(3)-C(8)-C(9)-C(10) | 60.79(13) |
| C(12)-C(8)-C(9)-Ru(3) | -60.87(13) |
| C(8)-C(9)-C(10)-C(11) | 1.4(2) |
| Ru(3)-C(9)-C(10)-C(11) | 63.58(13) |
| C(8)-C(9)-C(10)-Ru(3) | -62.18(13) |
| C(9)-C(10)-C(11)-C(12) | -2.2(2) |
| Ru(3)-C(10)-C(11)-C(12) | 61.96(13) |
| C(9)-C(10)-C(11)-Ru(3) | -64.15(13) |
| C(10)-C(11)-C(12)-C(8) | 2.1(2) |
| Ru(3)-C(11)-C(12)-C(8) | 63.66(13) |
| C(10)-C(11)-C(12)-Ru(3) | -61.52(13) |
| C(9)-C(8)-C(12)-C(11) | -1.3(2) |
| Ru(3)-C(8)-C(12)-C(11) | -62.93(12) |
| C(9)-C(8)-C(12)-Ru(3) | 61.66(13) |
| O(2)-C(7)-Ru(1)-C(6) | 162(2) |
| O(2)-C(7)-Ru(1)-C(4) | 50(2) |
| O(2)-C(7)-Ru(1)-C(2) | 4(3) |
| O(2)-C(7)-Ru(1)-C(3) | 66(2) |
| O(2)-C(7)-Ru(1)-C(1) | -15(2) |
| O(2)-C(7)-Ru(1)-C(5) | 12(2) |

| | |
|---|---|
| O(2)-C(7)-Ru(1)-I(1) | -107(2) |
| O(1)-C(6)-Ru(1)-C(7) | -124(3) |
| O(1)-C(6)-Ru(1)-C(4) | -20(3) |
| O(1)-C(6)-Ru(1)-C(2) | 48(3) |
| O(1)-C(6)-Ru(1)-C(3) | 14(3) |
| O(1)-C(6)-Ru(1)-C(1) | 52(3) |
| O(1)-C(6)-Ru(1)-C(5) | -19(3) |
| O(1)-C(6)-Ru(1)-I(1) | 145(3) |
| C(3)-C(4)-Ru(1)-C(7) | 160.99(13) |
| C(5)-C(4)-Ru(1)-C(7) | -83.55(13) |
| C(3)-C(4)-Ru(1)-C(6) | 63.88(14) |
| C(5)-C(4)-Ru(1)-C(6) | 179.35(12) |
| C(3)-C(4)-Ru(1)-C(2) | -36.49(13) |
| C(5)-C(4)-Ru(1)-C(2) | 78.98(13) |
| C(5)-C(4)-Ru(1)-C(3) | 115.47(18) |
| C(3)-C(4)-Ru(1)-C(1) | -79.33(13) |
| C(5)-C(4)-Ru(1)-C(1) | 36.13(12) |
| C(3)-C(4)-Ru(1)-C(5) | -115.47(18) |
| C(3)-C(4)-Ru(1)-I(1) | -80.08(16) |
| C(5)-C(4)-Ru(1)-I(1) | 35.39(19) |
| C(3)-C(2)-Ru(1)-C(7) | 88.3(2) |
| C(1)-C(2)-Ru(1)-C(7) | -27.6(3) |
| C(3)-C(2)-Ru(1)-C(6) | -68.39(12) |
| C(1)-C(2)-Ru(1)-C(6) | 175.68(12) |
| C(3)-C(2)-Ru(1)-C(4) | 36.95(11) |
| C(1)-C(2)-Ru(1)-C(4) | -78.98(12) |
| C(1)-C(2)-Ru(1)-C(3) | -115.93(16) |
| C(3)-C(2)-Ru(1)-C(1) | 115.93(16) |
| C(3)-C(2)-Ru(1)-C(5) | 79.36(12) |
| C(1)-C(2)-Ru(1)-C(5) | -36.57(11) |
| C(3)-C(2)-Ru(1)-I(1) | -161.32(10) |
| C(1)-C(2)-Ru(1)-I(1) | 82.76(11) |
| C(2)-C(3)-Ru(1)-C(7) | -146.48(13) |
| C(4)-C(3)-Ru(1)-C(7) | -27.93(17) |
| C(2)-C(3)-Ru(1)-C(6) | 118.09(12) |
| C(4)-C(3)-Ru(1)-C(6) | -123.35(13) |
| C(2)-C(3)-Ru(1)-C(4) | -118.55(17) |
| C(4)-C(3)-Ru(1)-C(2) | 118.55(17) |

| | |
|---|---|
| C(2)-C(3)-Ru(1)-C(1) | -38.63(12) |
| C(4)-C(3)-Ru(1)-C(1) | 79.93(13) |
| C(2)-C(3)-Ru(1)-C(5) | -80.10(13) |
| C(4)-C(3)-Ru(1)-C(5) | 38.45(12) |
| C(2)-C(3)-Ru(1)-I(1) | 25.09(14) |
| C(4)-C(3)-Ru(1)-I(1) | 143.64(10) |
| C(5)-C(1)-Ru(1)-C(7) | 50.70(14) |
| C(2)-C(1)-Ru(1)-C(7) | 168.19(12) |
| C(5)-C(1)-Ru(1)-C(6) | -124.85(14) |
| C(2)-C(1)-Ru(1)-C(6) | -7.4(2) |
| C(5)-C(1)-Ru(1)-C(4) | -37.11(11) |
| C(2)-C(1)-Ru(1)-C(4) | 80.39(13) |
| C(5)-C(1)-Ru(1)-C(2) | -117.49(17) |
| C(5)-C(1)-Ru(1)-C(3) | -79.70(12) |
| C(2)-C(1)-Ru(1)-C(3) | 37.79(12) |
| C(2)-C(1)-Ru(1)-C(5) | 117.49(17) |
| C(5)-C(1)-Ru(1)-I(1) | 142.56(11) |
| C(2)-C(1)-Ru(1)-I(1) | -99.95(11) |
| C(1)-C(5)-Ru(1)-C(7) | -138.68(12) |
| C(4)-C(5)-Ru(1)-C(7) | 102.79(13) |
| C(1)-C(5)-Ru(1)-C(6) | 117.35(16) |
| C(4)-C(5)-Ru(1)-C(6) | -1.2(2) |
| C(1)-C(5)-Ru(1)-C(4) | 118.54(17) |
| C(1)-C(5)-Ru(1)-C(2) | 37.94(12) |
| C(4)-C(5)-Ru(1)-C(2) | -80.59(13) |
| C(1)-C(5)-Ru(1)-C(3) | 80.04(13) |
| C(4)-C(5)-Ru(1)-C(3) | -38.50(12) |
| C(4)-C(5)-Ru(1)-C(1) | -118.54(17) |
| C(1)-C(5)-Ru(1)-I(1) | -44.06(12) |
| C(4)-C(5)-Ru(1)-I(1) | -162.60(10) |
| O(3)-C(13)-Ru(3)-C(14) | -145(2) |
| O(3)-C(13)-Ru(3)-C(10) | -46(2) |
| O(3)-C(13)-Ru(3)-C(11) | -14(2) |
| O(3)-C(13)-Ru(3)-C(12) | 22(2) |
| O(3)-C(13)-Ru(3)-C(9) | -42(2) |
| O(3)-C(13)-Ru(3)-C(8) | 30(2) |
| O(3)-C(13)-Ru(3)-I(1) | 122(2) |
| O(4)-C(14)-Ru(3)-C(13) | 144.4(17) |

| | |
|---|---|
| O(4)-C(14)-Ru(3)-C(10) | 29.5(17) |
| O(4)-C(14)-Ru(3)-C(11) | 47.9(18) |
| O(4)-C(14)-Ru(3)-C(12) | -3.2(19) |
| O(4)-C(14)-Ru(3)-C(9) | -8.0(17) |
| O(4)-C(14)-Ru(3)-C(8) | -32.0(18) |
| O(4)-C(14)-Ru(3)-I(1) | -125.6(17) |
| C(11)-C(10)-Ru(3)-C(13) | 61.26(13) |
| C(9)-C(10)-Ru(3)-C(13) | 177.35(11) |
| C(11)-C(10)-Ru(3)-C(14) | 157.12(12) |
| C(9)-C(10)-Ru(3)-C(14) | -86.80(12) |
| C(9)-C(10)-Ru(3)-C(11) | 116.09(17) |
| C(11)-C(10)-Ru(3)-C(12) | -37.23(12) |
| C(9)-C(10)-Ru(3)-C(12) | 78.86(12) |
| C(11)-C(10)-Ru(3)-C(9) | -116.09(17) |
| C(11)-C(10)-Ru(3)-C(8) | -79.69(13) |
| C(9)-C(10)-Ru(3)-C(8) | 36.40(11) |
| C(11)-C(10)-Ru(3)-I(1) | -90.37(16) |
| C(9)-C(10)-Ru(3)-I(1) | 25.7(2) |
| C(12)-C(11)-Ru(3)-C(13) | 115.51(12) |
| C(10)-C(11)-Ru(3)-C(13) | -126.81(12) |
| C(12)-C(11)-Ru(3)-C(14) | -148.53(12) |
| C(10)-C(11)-Ru(3)-C(14) | -30.85(16) |
| C(12)-C(11)-Ru(3)-C(10) | -117.68(17) |
| C(10)-C(11)-Ru(3)-C(12) | 117.68(17) |
| C(12)-C(11)-Ru(3)-C(9) | -79.51(12) |
| C(10)-C(11)-Ru(3)-C(9) | 38.16(11) |
| C(12)-C(11)-Ru(3)-C(8) | -38.07(11) |
| C(10)-C(11)-Ru(3)-C(8) | 79.60(12) |
| C(12)-C(11)-Ru(3)-I(1) | 22.25(15) |
| C(10)-C(11)-Ru(3)-I(1) | 139.92(10) |
| C(11)-C(12)-Ru(3)-C(13) | -71.26(13) |
| C(8)-C(12)-Ru(3)-C(13) | 172.46(11) |
| C(11)-C(12)-Ru(3)-C(14) | 74.5(2) |
| C(8)-C(12)-Ru(3)-C(14) | -41.8(2) |
| C(11)-C(12)-Ru(3)-C(10) | 37.39(12) |
| C(8)-C(12)-Ru(3)-C(10) | -78.90(12) |
| C(8)-C(12)-Ru(3)-C(11) | -116.29(16) |
| C(11)-C(12)-Ru(3)-C(9) | 79.91(13) |

| | |
|---|---|
| C(8)-C(12)-Ru(3)-C(9) | -36.38(11) |
| C(11)-C(12)-Ru(3)-C(8) | 116.29(16) |
| C(11)-C(12)-Ru(3)-I(1) | -164.26(11) |
| C(8)-C(12)-Ru(3)-I(1) | 79.45(11) |
| C(8)-C(9)-Ru(3)-C(13) | 112.98(17) |
| C(10)-C(9)-Ru(3)-C(13) | -5.1(2) |
| C(8)-C(9)-Ru(3)-C(14) | -144.86(12) |
| C(10)-C(9)-Ru(3)-C(14) | 97.06(12) |
| C(8)-C(9)-Ru(3)-C(10) | 118.08(17) |
| C(8)-C(9)-Ru(3)-C(11) | 79.86(13) |
| C(10)-C(9)-Ru(3)-C(11) | -38.22(12) |
| C(8)-C(9)-Ru(3)-C(12) | 37.36(11) |
| C(10)-C(9)-Ru(3)-C(12) | -80.72(13) |
| C(10)-C(9)-Ru(3)-C(8) | -118.08(17) |
| C(8)-C(9)-Ru(3)-I(1) | -49.10(12) |
| C(10)-C(9)-Ru(3)-I(1) | -167.18(10) |
| C(9)-C(8)-Ru(3)-C(13) | -130.68(14) |
| C(12)-C(8)-Ru(3)-C(13) | -12.54(18) |
| C(9)-C(8)-Ru(3)-C(14) | 43.02(14) |
| C(12)-C(8)-Ru(3)-C(14) | 161.17(11) |
| C(9)-C(8)-Ru(3)-C(10) | -37.42(12) |
| C(12)-C(8)-Ru(3)-C(10) | 80.72(12) |
| C(9)-C(8)-Ru(3)-C(11) | -80.13(13) |
| C(12)-C(8)-Ru(3)-C(11) | 38.01(11) |
| C(9)-C(8)-Ru(3)-C(12) | -118.14(17) |
| C(12)-C(8)-Ru(3)-C(9) | 118.14(17) |
| C(9)-C(8)-Ru(3)-I(1) | 137.74(11) |
| C(12)-C(8)-Ru(3)-I(1) | -104.12(10) |
| C(7)-Ru(1)-I(1)-Ru(3) | 40.90(5) |
| C(6)-Ru(1)-I(1)-Ru(3) | 132.70(5) |
| C(4)-Ru(1)-I(1)-Ru(3) | -80.45(12) |
| C(2)-Ru(1)-I(1)-Ru(3) | -118.52(6) |
| C(3)-Ru(1)-I(1)-Ru(3) | -133.39(7) |
| C(1)-Ru(1)-I(1)-Ru(3) | -81.11(6) |
| C(5)-Ru(1)-I(1)-Ru(3) | -56.74(6) |
| C(13)-Ru(3)-I(1)-Ru(1) | 127.10(5) |
| C(14)-Ru(3)-I(1)-Ru(1) | 34.86(5) |
| C(10)-Ru(3)-I(1)-Ru(1) | -78.57(13) |

| | |
|---|---|
| C(11)-Ru(3)-I(1)-Ru(1) | -138.21(7) |
| C(12)-Ru(3)-I(1)-Ru(1) | -124.72(5) |
| C(9)-Ru(3)-I(1)-Ru(1) | -61.29(6) |
| C(8)-Ru(3)-I(1)-Ru(1) | -88.00(5) |

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Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2  #2 -x+2,y,-z+1/2

## POLYMORPH II - $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2I\}$

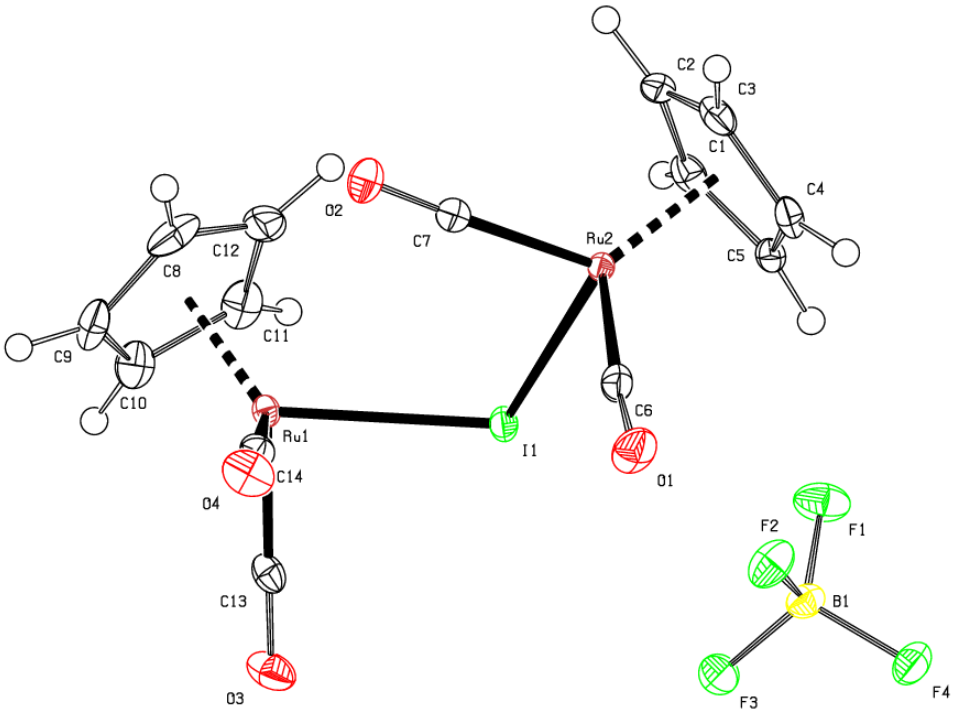

**Table B7:** Crystal data and structure refinement for $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2I\}$.

| | | |
|---|---|---|
| Identification code | 12bo_hbf_ne4_0m | |
| Empirical formula | C14 H10 B F4 I N0 O4 Ru2 | |
| Formula weight | 658.07 | |
| Temperature | 446(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P21/c | |
| Unit cell dimensions | a = 7.00560(10) Å | α= 90°. |
| | b = 14.1446(3) Å | β= 96.2390(10)°. |
| | c = 18.2226(3) Å | γ = 90°. |
| Volume | 1795.01(5) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 2.435 $Mg/m^3$ | |
| Absorption coefficient | 3.458 $mm^{-1}$ | |
| F(000) | 1232 | |
| Crystal size | 0.42 x 0.16 x 0.11 $mm^3$ | |
| Theta range for data collection | 1.83 to 28.32°. | |
| Index ranges | -8<=h<=9, -18<=k<=18, -24<=l<=22 | |
| Reflections collected | 42242 | |
| Independent reflections | 4471 [R(int) = 0.0244] | |
| Completeness to theta = 28.32° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7022 and 0.3245 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4471 / 28 / 235 | |
| Goodness-of-fit on $F^2$ | 1.111 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0127, wR2 = 0.0322 | |
| R indices (all data) | R1 = 0.0135, wR2 = 0.0326 | |
| Largest diff. peak and hole | 0.462 and -0.621 $e.Å^{-3}$ | |

**Table B8:** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for {[$\eta^5$-$C_5H_5Ru(CO)_2]_2I$}. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 4014(2) | 8243(1) | 7555(1) | 18(1) |
| C(2) | 3295(2) | 9160(1) | 7404(1) | 21(1) |
| C(3) | 4873(3) | 9809(1) | 7484(1) | 20(1) |
| C(4) | 6556(2) | 9277(1) | 7715(1) | 18(1) |
| C(5) | 6054(2) | 8311(1) | 7743(1) | 15(1) |
| C(6) | 7727(2) | 9153(1) | 6220(1) | 18(1) |
| C(7) | 3901(2) | 9352(1) | 5764(1) | 15(1) |
| C(8) | 410(2) | 7769(1) | 4516(1) | 28(1) |
| C(9) | 513(2) | 7065(1) | 3957(1) | 24(1) |
| C(10) | 602(2) | 6171(1) | 4308(1) | 23(1) |
| C(11) | 626(2) | 6314(1) | 5080(1) | 24(1) |
| C(12) | 493(2) | 7308(2) | 5201(1) | 28(1) |
| C(13) | 4909(2) | 6028(1) | 4444(1) | 17(1) |
| C(14) | 4712(2) | 7916(1) | 4265(1) | 16(1) |
| B(1) | 9983(2) | 6359(1) | 7357(1) | 18(1) |
| O(1) | 9172(2) | 9366(1) | 6044(1) | 27(1) |
| O(2) | 2971(2) | 9684(1) | 5281(1) | 22(1) |
| O(3) | 5913(2) | 5434(1) | 4306(1) | 26(1) |
| O(4) | 5562(2) | 8472(1) | 3990(1) | 26(1) |
| F(1) | 8461(2) | 6303(1) | 7784(1) | 29(1) |
| F(2) | 10002(1) | 7257(1) | 7037(1) | 26(1) |
| F(3) | 9782(2) | 5663(1) | 6809(1) | 26(1) |
| F(4) | 11708(1) | 6222(1) | 7806(1) | 24(1) |
| Ru(1) | 3216(1) | 6986(1) | 4695(1) | 11(1) |
| Ru(2) | 5394(1) | 8821(1) | 6593(1) | 10(1) |
| I(1) | 5423(1) | 7082(1) | 5995(1) | 16(1) |

**Table B9:** Bond lengths [Å] and angles [°] for $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2I\}$.

| | |
|---|---|
| C(1)-C(2) | 1.409(2) |
| C(1)-C(5) | 1.436(2) |
| C(1)-Ru(2) | 2.2457(15) |
| C(1)-H(1) | 0.9800 |
| C(2)-C(3) | 1.431(2) |
| C(2)-Ru(2) | 2.2477(15) |
| C(2)-H(2) | 0.9800 |
| C(3)-C(4) | 1.423(2) |
| C(3)-Ru(2) | 2.2025(15) |
| C(3)-H(3) | 0.9800 |
| C(4)-C(5) | 1.413(2) |
| C(4)-Ru(2) | 2.2123(14) |
| C(4)-H(4) | 0.9800 |
| C(5)-Ru(2) | 2.2178(14) |
| C(5)-H(5) | 0.9800 |
| C(6)-O(1) | 1.135(2) |
| C(6)-Ru(2) | 1.8958(16) |
| C(7)-O(2) | 1.1383(19) |
| C(7)-Ru(2) | 1.8959(15) |
| C(8)-C(12) | 1.404(3) |
| C(8)-C(9) | 1.432(3) |
| C(8)-Ru(1) | 2.2488(17) |
| C(8)-H(8) | 0.9800 |
| C(9)-C(10) | 1.416(2) |
| C(9)-Ru(1) | 2.2027(16) |
| C(9)-H(9) | 0.9800 |
| C(10)-C(11) | 1.419(3) |
| C(10)-Ru(1) | 2.2133(16) |
| C(10)-H(10) | 0.9800 |
| C(11)-C(12) | 1.428(3) |
| C(11)-Ru(1) | 2.2283(16) |
| C(11)-H(11) | 0.9800 |
| C(12)-Ru(1) | 2.2537(17) |
| C(12)-H(12) | 0.9800 |
| C(13)-O(3) | 1.141(2) |

| | |
|---|---|
| C(13)-Ru(1) | 1.8897(16) |
| C(14)-O(4) | 1.1353(19) |
| C(14)-Ru(1) | 1.9029(16) |
| B(1)-F(1) | 1.389(2) |
| B(1)-F(4) | 1.397(2) |
| B(1)-F(2) | 1.398(2) |
| B(1)-F(3) | 1.398(2) |
| Ru(1)-I(1) | 2.68768(15) |
| Ru(2)-I(1) | 2.69093(15) |

| | |
|---|---|
| C(2)-C(1)-C(5) | 108.08(14) |
| C(2)-C(1)-Ru(2) | 71.81(9) |
| C(5)-C(1)-Ru(2) | 70.18(8) |
| C(2)-C(1)-H(1) | 125.9 |
| C(5)-C(1)-H(1) | 125.9 |
| Ru(2)-C(1)-H(1) | 125.9 |
| C(1)-C(2)-C(3) | 108.34(14) |
| C(1)-C(2)-Ru(2) | 71.66(9) |
| C(3)-C(2)-Ru(2) | 69.53(9) |
| C(1)-C(2)-H(2) | 125.8 |
| C(3)-C(2)-H(2) | 125.8 |
| Ru(2)-C(2)-H(2) | 125.8 |
| C(4)-C(3)-C(2) | 107.30(14) |
| C(4)-C(3)-Ru(2) | 71.57(9) |
| C(2)-C(3)-Ru(2) | 72.96(9) |
| C(4)-C(3)-H(3) | 126.2 |
| C(2)-C(3)-H(3) | 126.2 |
| Ru(2)-C(3)-H(3) | 126.2 |
| C(5)-C(4)-C(3) | 108.69(14) |
| C(5)-C(4)-Ru(2) | 71.61(8) |
| C(3)-C(4)-Ru(2) | 70.82(9) |
| C(5)-C(4)-H(4) | 125.6 |
| C(3)-C(4)-H(4) | 125.6 |
| Ru(2)-C(4)-H(4) | 125.6 |
| C(4)-C(5)-C(1) | 107.52(13) |
| C(4)-C(5)-Ru(2) | 71.18(8) |
| C(1)-C(5)-Ru(2) | 72.29(8) |
| C(4)-C(5)-H(5) | 126.1 |

| | |
|---|---|
| C(1)-C(5)-H(5) | 126.1 |
| Ru(2)-C(5)-H(5) | 126.1 |
| O(1)-C(6)-Ru(2) | 175.36(14) |
| O(2)-C(7)-Ru(2) | 177.94(14) |
| C(12)-C(8)-C(9) | 107.99(16) |
| C(12)-C(8)-Ru(1) | 72.01(10) |
| C(9)-C(8)-Ru(1) | 69.50(10) |
| C(12)-C(8)-H(8) | 126.0 |
| C(9)-C(8)-H(8) | 126.0 |
| Ru(1)-C(8)-H(8) | 126.0 |
| C(10)-C(9)-C(8) | 107.67(15) |
| C(10)-C(9)-Ru(1) | 71.70(10) |
| C(8)-C(9)-Ru(1) | 73.00(10) |
| C(10)-C(9)-H(9) | 126.0 |
| C(8)-C(9)-H(9) | 126.0 |
| Ru(1)-C(9)-H(9) | 126.0 |
| C(9)-C(10)-C(11) | 108.37(15) |
| C(9)-C(10)-Ru(1) | 70.89(9) |
| C(11)-C(10)-Ru(1) | 71.94(9) |
| C(9)-C(10)-H(10) | 125.8 |
| C(11)-C(10)-H(10) | 125.8 |
| Ru(1)-C(10)-H(10) | 125.8 |
| C(10)-C(11)-C(12) | 107.45(15) |
| C(10)-C(11)-Ru(1) | 70.79(9) |
| C(12)-C(11)-Ru(1) | 72.38(10) |
| C(10)-C(11)-H(11) | 126.2 |
| C(12)-C(11)-H(11) | 126.2 |
| Ru(1)-C(11)-H(11) | 126.2 |
| C(8)-C(12)-C(11) | 108.47(16) |
| C(8)-C(12)-Ru(1) | 71.64(10) |
| C(11)-C(12)-Ru(1) | 70.46(10) |
| C(8)-C(12)-H(12) | 125.7 |
| C(11)-C(12)-H(12) | 125.7 |
| Ru(1)-C(12)-H(12) | 125.7 |
| O(3)-C(13)-Ru(1) | 178.23(14) |
| O(4)-C(14)-Ru(1) | 177.84(15) |
| F(1)-B(1)-F(4) | 109.37(14) |
| F(1)-B(1)-F(2) | 109.14(13) |

| | |
|---|---|
| F(4)-B(1)-F(2) | 108.87(13) |
| F(1)-B(1)-F(3) | 109.62(13) |
| F(4)-B(1)-F(3) | 109.52(13) |
| F(2)-B(1)-F(3) | 110.29(14) |
| C(13)-Ru(1)-C(14) | 90.42(7) |
| C(13)-Ru(1)-C(9) | 114.16(7) |
| C(14)-Ru(1)-C(9) | 100.91(7) |
| C(13)-Ru(1)-C(10) | 93.92(7) |
| C(14)-Ru(1)-C(10) | 134.65(7) |
| C(9)-Ru(1)-C(10) | 37.41(6) |
| C(13)-Ru(1)-C(11) | 108.91(7) |
| C(14)-Ru(1)-C(11) | 158.22(7) |
| C(9)-Ru(1)-C(11) | 62.52(6) |
| C(10)-Ru(1)-C(11) | 37.27(7) |
| C(13)-Ru(1)-C(8) | 151.63(7) |
| C(14)-Ru(1)-C(8) | 96.44(7) |
| C(9)-Ru(1)-C(8) | 37.50(7) |
| C(10)-Ru(1)-C(8) | 62.02(7) |
| C(11)-Ru(1)-C(8) | 61.78(7) |
| C(13)-Ru(1)-C(12) | 145.63(7) |
| C(14)-Ru(1)-C(12) | 123.91(7) |
| C(9)-Ru(1)-C(12) | 61.96(7) |
| C(10)-Ru(1)-C(12) | 61.85(7) |
| C(11)-Ru(1)-C(12) | 37.16(7) |
| C(8)-Ru(1)-C(12) | 36.35(7) |
| C(13)-Ru(1)-I(1) | 86.17(5) |
| C(14)-Ru(1)-I(1) | 92.19(5) |
| C(9)-Ru(1)-I(1) | 155.41(5) |
| C(10)-Ru(1)-I(1) | 133.13(5) |
| C(11)-Ru(1)-I(1) | 98.86(4) |
| C(8)-Ru(1)-I(1) | 120.86(5) |
| C(12)-Ru(1)-I(1) | 93.46(5) |
| C(6)-Ru(2)-C(7) | 92.22(6) |
| C(6)-Ru(2)-C(3) | 109.01(7) |
| C(7)-Ru(2)-C(3) | 102.38(6) |
| C(6)-Ru(2)-C(4) | 90.81(6) |
| C(7)-Ru(2)-C(4) | 137.39(6) |
| C(3)-Ru(2)-C(4) | 37.61(6) |

| | |
|---|---|
| C(6)-Ru(2)-C(5) | 108.68(6) |
| C(7)-Ru(2)-C(5) | 157.21(6) |
| C(3)-Ru(2)-C(5) | 62.85(6) |
| C(4)-Ru(2)-C(5) | 37.21(6) |
| C(6)-Ru(2)-C(1) | 146.20(6) |
| C(7)-Ru(2)-C(1) | 121.24(6) |
| C(3)-Ru(2)-C(1) | 62.33(6) |
| C(4)-Ru(2)-C(1) | 62.06(6) |
| C(5)-Ru(2)-C(1) | 37.54(6) |
| C(6)-Ru(2)-C(2) | 146.51(7) |
| C(7)-Ru(2)-C(2) | 95.47(6) |
| C(3)-Ru(2)-C(2) | 37.50(6) |
| C(4)-Ru(2)-C(2) | 62.05(6) |
| C(5)-Ru(2)-C(2) | 62.08(6) |
| C(1)-Ru(2)-C(2) | 36.54(6) |
| C(6)-Ru(2)-I(1) | 92.10(5) |
| C(7)-Ru(2)-I(1) | 93.87(5) |
| C(3)-Ru(2)-I(1) | 152.55(4) |
| C(4)-Ru(2)-I(1) | 128.48(4) |
| C(5)-Ru(2)-I(1) | 94.32(4) |
| C(1)-Ru(2)-I(1) | 90.34(4) |
| C(2)-Ru(2)-I(1) | 119.72(5) |
| Ru(1)-I(1)-Ru(2) | 111.979(5) |

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Symmetry transformations used to generate equivalent atoms:

**Table B10:** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for {[$\eta^5$-$C_5H_5Ru(CO)_2$]$_2$I}. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 19(1) | 22(1) | 14(1) | -1(1) | 6(1) | -7(1) |
| C(2) | 17(1) | 33(1) | 14(1) | -2(1) | 4(1) | 9(1) |
| C(3) | 33(1) | 15(1) | 13(1) | -2(1) | 3(1) | 4(1) |
| C(4) | 20(1) | 22(1) | 11(1) | -3(1) | 0(1) | -5(1) |
| C(5) | 18(1) | 17(1) | 10(1) | 2(1) | 2(1) | 2(1) |
| C(6) | 18(1) | 23(1) | 14(1) | 1(1) | -1(1) | 1(1) |
| C(7) | 15(1) | 14(1) | 16(1) | 0(1) | 3(1) | -2(1) |
| C(8) | 13(1) | 21(1) | 49(1) | 3(1) | -3(1) | 2(1) |
| C(9) | 17(1) | 35(1) | 20(1) | 8(1) | -5(1) | -6(1) |
| C(10) | 19(1) | 23(1) | 27(1) | -3(1) | -2(1) | -9(1) |
| C(11) | 19(1) | 30(1) | 23(1) | 8(1) | 2(1) | -8(1) |
| C(12) | 14(1) | 41(1) | 28(1) | -11(1) | 4(1) | 0(1) |
| C(13) | 24(1) | 15(1) | 11(1) | 1(1) | 3(1) | -1(1) |
| C(14) | 18(1) | 14(1) | 16(1) | -2(1) | 2(1) | 1(1) |
| B(1) | 14(1) | 15(1) | 23(1) | -2(1) | 1(1) | 0(1) |
| O(1) | 16(1) | 41(1) | 26(1) | 7(1) | 5(1) | -2(1) |
| O(2) | 22(1) | 22(1) | 19(1) | 5(1) | -3(1) | 1(1) |
| O(3) | 39(1) | 19(1) | 21(1) | 2(1) | 11(1) | 8(1) |
| O(4) | 31(1) | 19(1) | 30(1) | 1(1) | 11(1) | -6(1) |
| F(1) | 23(1) | 25(1) | 40(1) | -5(1) | 14(1) | -4(1) |
| F(2) | 22(1) | 20(1) | 35(1) | 7(1) | -3(1) | -1(1) |
| F(3) | 27(1) | 24(1) | 27(1) | -10(1) | -3(1) | 4(1) |
| F(4) | 20(1) | 21(1) | 28(1) | -1(1) | -6(1) | 3(1) |
| Ru(1) | 14(1) | 10(1) | 10(1) | 0(1) | 1(1) | -1(1) |
| Ru(2) | 10(1) | 11(1) | 10(1) | 0(1) | 0(1) | 0(1) |
| I(1) | 20(1) | 14(1) | 13(1) | -2(1) | -4(1) | 4(1) |

**Table B11:** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for {[$\eta^5$-$C_5H_5Ru(CO)_2]_2I$}.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 3248 | 7663 | 7554 | 21 |
| H(2) | 1942 | 9329 | 7280 | 25 |
| H(3) | 4788 | 10499 | 7444 | 24 |
| H(4) | 7839 | 9540 | 7852 | 21 |
| H(5) | 6921 | 7790 | 7906 | 18 |
| H(8) | 254 | 8451 | 4433 | 34 |
| H(9) | 395 | 7177 | 3424 | 29 |
| H(10) | 574 | 5556 | 4058 | 28 |
| H(11) | 621 | 5819 | 5456 | 29 |
| H(12) | 416 | 7615 | 5679 | 33 |

**Table B12:** Torsion angles [°] for {[$\eta^5$-$C_5H_5Ru(CO)_2]_2I$}$BF_4$.

| | |
|---|---|
| C(5)-C(1)-C(2)-C(3) | 1.00(17) |
| Ru(2)-C(1)-C(2)-C(3) | -60.13(10) |
| C(5)-C(1)-C(2)-Ru(2) | 61.13(10) |
| C(1)-C(2)-C(3)-C(4) | -2.31(17) |
| Ru(2)-C(2)-C(3)-C(4) | -63.78(10) |
| C(1)-C(2)-C(3)-Ru(2) | 61.47(11) |
| C(2)-C(3)-C(4)-C(5) | 2.76(17) |
| Ru(2)-C(3)-C(4)-C(5) | -61.95(10) |
| C(2)-C(3)-C(4)-Ru(2) | 64.71(10) |
| C(3)-C(4)-C(5)-C(1) | -2.16(17) |
| Ru(2)-C(4)-C(5)-C(1) | -63.60(10) |
| C(3)-C(4)-C(5)-Ru(2) | 61.45(10) |
| C(2)-C(1)-C(5)-C(4) | 0.71(16) |
| Ru(2)-C(1)-C(5)-C(4) | 62.88(10) |
| C(2)-C(1)-C(5)-Ru(2) | -62.17(10) |
| C(12)-C(8)-C(9)-C(10) | 1.7(2) |
| Ru(1)-C(8)-C(9)-C(10) | 63.77(12) |

| | |
|---|---|
| C(12)-C(8)-C(9)-Ru(1) | -62.09(12) |
| C(8)-C(9)-C(10)-C(11) | -2.1(2) |
| Ru(1)-C(9)-C(10)-C(11) | 62.56(12) |
| C(8)-C(9)-C(10)-Ru(1) | -64.62(12) |
| C(9)-C(10)-C(11)-C(12) | 1.7(2) |
| Ru(1)-C(10)-C(11)-C(12) | 63.55(12) |
| C(9)-C(10)-C(11)-Ru(1) | -61.89(12) |
| C(9)-C(8)-C(12)-C(11) | -0.7(2) |
| Ru(1)-C(8)-C(12)-C(11) | -61.15(12) |
| C(9)-C(8)-C(12)-Ru(1) | 60.49(12) |
| C(10)-C(11)-C(12)-C(8) | -0.6(2) |
| Ru(1)-C(11)-C(12)-C(8) | 61.90(12) |
| C(10)-C(11)-C(12)-Ru(1) | -62.50(12) |
| O(3)-C(13)-Ru(1)-C(14) | 162(5) |
| O(3)-C(13)-Ru(1)-C(9) | -96(5) |
| O(3)-C(13)-Ru(1)-C(10) | -63(5) |
| O(3)-C(13)-Ru(1)-C(11) | -28(5) |
| O(3)-C(13)-Ru(1)-C(8) | -93(5) |
| O(3)-C(13)-Ru(1)-C(12) | -21(5) |
| O(3)-C(13)-Ru(1)-I(1) | 70(5) |
| O(4)-C(14)-Ru(1)-C(13) | 106(4) |
| O(4)-C(14)-Ru(1)-C(9) | -9(4) |
| O(4)-C(14)-Ru(1)-C(10) | 10(4) |
| O(4)-C(14)-Ru(1)-C(11) | -47(4) |
| O(4)-C(14)-Ru(1)-C(8) | -46(4) |
| O(4)-C(14)-Ru(1)-C(12) | -72(4) |
| O(4)-C(14)-Ru(1)-I(1) | -168(4) |
| C(10)-C(9)-Ru(1)-C(13) | 62.40(12) |
| C(8)-C(9)-Ru(1)-C(13) | 178.21(10) |
| C(10)-C(9)-Ru(1)-C(14) | 157.83(11) |
| C(8)-C(9)-Ru(1)-C(14) | -86.36(11) |
| C(8)-C(9)-Ru(1)-C(10) | 115.82(15) |
| C(10)-C(9)-Ru(1)-C(11) | -37.21(11) |
| C(8)-C(9)-Ru(1)-C(11) | 78.60(12) |
| C(10)-C(9)-Ru(1)-C(8) | -115.82(15) |
| C(10)-C(9)-Ru(1)-C(12) | -79.42(12) |
| C(8)-C(9)-Ru(1)-C(12) | 36.40(11) |
| C(10)-C(9)-Ru(1)-I(1) | -81.19(15) |

| | |
|---|---|
| C(8)-C(9)-Ru(1)-I(1) | 34.63(17) |
| C(9)-C(10)-Ru(1)-C(13) | -125.86(11) |
| C(11)-C(10)-Ru(1)-C(13) | 116.51(11) |
| C(9)-C(10)-Ru(1)-C(14) | -31.39(15) |
| C(11)-C(10)-Ru(1)-C(14) | -149.02(11) |
| C(11)-C(10)-Ru(1)-C(9) | -117.63(16) |
| C(9)-C(10)-Ru(1)-C(11) | 117.63(16) |
| C(9)-C(10)-Ru(1)-C(8) | 38.36(11) |
| C(11)-C(10)-Ru(1)-C(8) | -79.28(12) |
| C(9)-C(10)-Ru(1)-C(12) | 79.76(12) |
| C(11)-C(10)-Ru(1)-C(12) | -37.87(11) |
| C(9)-C(10)-Ru(1)-I(1) | 145.71(9) |
| C(11)-C(10)-Ru(1)-I(1) | 28.08(13) |
| C(10)-C(11)-Ru(1)-C(13) | -70.68(11) |
| C(12)-C(11)-Ru(1)-C(13) | 172.97(10) |
| C(10)-C(11)-Ru(1)-C(14) | 80.7(2) |
| C(12)-C(11)-Ru(1)-C(14) | -35.6(2) |
| C(10)-C(11)-Ru(1)-C(9) | 37.35(10) |
| C(12)-C(11)-Ru(1)-C(9) | -79.00(11) |
| C(12)-C(11)-Ru(1)-C(10) | -116.35(15) |
| C(10)-C(11)-Ru(1)-C(8) | 79.98(12) |
| C(12)-C(11)-Ru(1)-C(8) | -36.37(11) |
| C(10)-C(11)-Ru(1)-C(12) | 116.35(15) |
| C(10)-C(11)-Ru(1)-I(1) | -159.65(10) |
| C(12)-C(11)-Ru(1)-I(1) | 84.00(10) |
| C(12)-C(8)-Ru(1)-C(13) | 114.48(16) |
| C(9)-C(8)-Ru(1)-C(13) | -3.4(2) |
| C(12)-C(8)-Ru(1)-C(14) | -142.55(11) |
| C(9)-C(8)-Ru(1)-C(14) | 99.54(11) |
| C(12)-C(8)-Ru(1)-C(9) | 117.91(15) |
| C(12)-C(8)-Ru(1)-C(10) | 79.65(12) |
| C(9)-C(8)-Ru(1)-C(10) | -38.26(10) |
| C(12)-C(8)-Ru(1)-C(11) | 37.18(11) |
| C(9)-C(8)-Ru(1)-C(11) | -80.73(11) |
| C(9)-C(8)-Ru(1)-C(12) | -117.91(15) |
| C(12)-C(8)-Ru(1)-I(1) | -46.10(12) |
| C(9)-C(8)-Ru(1)-I(1) | -164.01(8) |
| C(8)-C(12)-Ru(1)-C(13) | -130.01(13) |

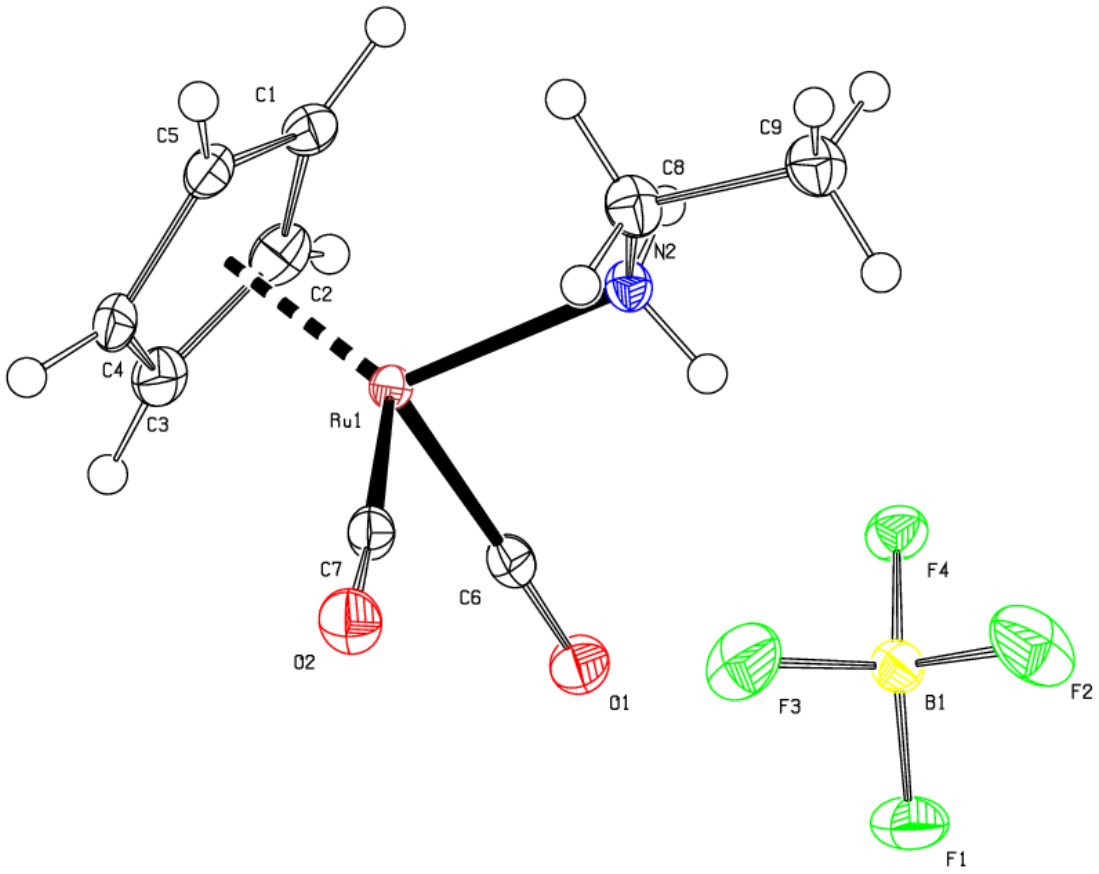
| | |
|---|---|
| C(11)-C(12)-Ru(1)-C(13) | -11.84(17) |
| C(8)-C(12)-Ru(1)-C(14) | 46.73(13) |
| C(11)-C(12)-Ru(1)-C(14) | 164.90(10) |
| C(8)-C(12)-Ru(1)-C(9) | -37.55(11) |
| C(11)-C(12)-Ru(1)-C(9) | 80.62(11) |
| C(8)-C(12)-Ru(1)-C(10) | -80.18(12) |
| C(11)-C(12)-Ru(1)-C(10) | 37.99(10) |
| C(8)-C(12)-Ru(1)-C(11) | -118.17(15) |
| C(11)-C(12)-Ru(1)-C(8) | 118.17(15) |
| C(8)-C(12)-Ru(1)-I(1) | 141.71(10) |
| C(11)-C(12)-Ru(1)-I(1) | -100.12(10) |
| O(1)-C(6)-Ru(2)-C(7) | 141.8(19) |
| O(1)-C(6)-Ru(2)-C(3) | 37.9(19) |
| O(1)-C(6)-Ru(2)-C(4) | 4.4(19) |
| O(1)-C(6)-Ru(2)-C(5) | -28.9(19) |
| O(1)-C(6)-Ru(2)-C(1) | -30.5(19) |
| O(1)-C(6)-Ru(2)-C(2) | 38.4(19) |
| O(1)-C(6)-Ru(2)-I(1) | -124.2(19) |
| O(2)-C(7)-Ru(2)-C(6) | -135(4) |
| O(2)-C(7)-Ru(2)-C(3) | -25(4) |
| O(2)-C(7)-Ru(2)-C(4) | -41(4) |
| O(2)-C(7)-Ru(2)-C(5) | 22(4) |
| O(2)-C(7)-Ru(2)-C(1) | 40(4) |
| O(2)-C(7)-Ru(2)-C(2) | 12(4) |
| O(2)-C(7)-Ru(2)-I(1) | 133(4) |
| C(4)-C(3)-Ru(2)-C(6) | -65.00(11) |
| C(2)-C(3)-Ru(2)-C(6) | 179.54(9) |
| C(4)-C(3)-Ru(2)-C(7) | -161.76(9) |
| C(2)-C(3)-Ru(2)-C(7) | 82.78(10) |
| C(2)-C(3)-Ru(2)-C(4) | -115.46(14) |
| C(4)-C(3)-Ru(2)-C(5) | 36.77(9) |
| C(2)-C(3)-Ru(2)-C(5) | -78.69(10) |
| C(4)-C(3)-Ru(2)-C(1) | 79.26(10) |
| C(2)-C(3)-Ru(2)-C(1) | -36.20(9) |
| C(4)-C(3)-Ru(2)-C(2) | 115.46(13) |
| C(4)-C(3)-Ru(2)-I(1) | 73.34(14) |
| C(2)-C(3)-Ru(2)-I(1) | -42.12(15) |
| C(5)-C(4)-Ru(2)-C(6) | -120.73(10) |

| | |
|---|---|
| C(3)-C(4)-Ru(2)-C(6) | 121.02(10) |
| C(5)-C(4)-Ru(2)-C(7) | 145.10(10) |
| C(3)-C(4)-Ru(2)-C(7) | 26.85(14) |
| C(5)-C(4)-Ru(2)-C(3) | 118.25(13) |
| C(3)-C(4)-Ru(2)-C(5) | -118.25(13) |
| C(5)-C(4)-Ru(2)-C(1) | 38.20(9) |
| C(3)-C(4)-Ru(2)-C(1) | -80.05(10) |
| C(5)-C(4)-Ru(2)-C(2) | 79.77(10) |
| C(3)-C(4)-Ru(2)-C(2) | -38.48(10) |
| C(5)-C(4)-Ru(2)-I(1) | -27.41(11) |
| C(3)-C(4)-Ru(2)-I(1) | -145.65(8) |
| C(4)-C(5)-Ru(2)-C(6) | 65.13(10) |
| C(1)-C(5)-Ru(2)-C(6) | -178.60(9) |
| C(4)-C(5)-Ru(2)-C(7) | -90.41(18) |
| C(1)-C(5)-Ru(2)-C(7) | 25.9(2) |
| C(4)-C(5)-Ru(2)-C(3) | -37.17(9) |
| C(1)-C(5)-Ru(2)-C(3) | 79.10(10) |
| C(1)-C(5)-Ru(2)-C(4) | 116.27(13) |
| C(4)-C(5)-Ru(2)-C(1) | -116.27(13) |
| C(4)-C(5)-Ru(2)-C(2) | -79.67(10) |
| C(1)-C(5)-Ru(2)-C(2) | 36.60(9) |
| C(4)-C(5)-Ru(2)-I(1) | 158.82(8) |
| C(1)-C(5)-Ru(2)-I(1) | -84.91(9) |
| C(2)-C(1)-Ru(2)-C(6) | 120.15(13) |
| C(5)-C(1)-Ru(2)-C(6) | 2.39(16) |
| C(2)-C(1)-Ru(2)-C(7) | -50.84(11) |
| C(5)-C(1)-Ru(2)-C(7) | -168.60(9) |
| C(2)-C(1)-Ru(2)-C(3) | 37.15(10) |
| C(5)-C(1)-Ru(2)-C(3) | -80.61(10) |
| C(2)-C(1)-Ru(2)-C(4) | 79.90(10) |
| C(5)-C(1)-Ru(2)-C(4) | -37.86(9) |
| C(2)-C(1)-Ru(2)-C(5) | 117.76(13) |
| C(5)-C(1)-Ru(2)-C(2) | -117.76(13) |
| C(2)-C(1)-Ru(2)-I(1) | -145.58(9) |
| C(5)-C(1)-Ru(2)-I(1) | 96.67(8) |
| C(1)-C(2)-Ru(2)-C(6) | -119.32(13) |
| C(3)-C(2)-Ru(2)-C(6) | -0.79(16) |
| C(1)-C(2)-Ru(2)-C(7) | 138.24(10) |

| | |
|---|---|
| C(3)-C(2)-Ru(2)-C(7) | -103.23(10) |
| C(1)-C(2)-Ru(2)-C(3) | -118.53(13) |
| C(1)-C(2)-Ru(2)-C(4) | -79.93(10) |
| C(3)-C(2)-Ru(2)-C(4) | 38.60(9) |
| C(1)-C(2)-Ru(2)-C(5) | -37.60(9) |
| C(3)-C(2)-Ru(2)-C(5) | 80.93(10) |
| C(3)-C(2)-Ru(2)-C(1) | 118.53(13) |
| C(1)-C(2)-Ru(2)-I(1) | 40.61(10) |
| C(3)-C(2)-Ru(2)-I(1) | 159.14(8) |
| C(13)-Ru(1)-I(1)-Ru(2) | 151.21(5) |
| C(14)-Ru(1)-I(1)-Ru(2) | 60.94(5) |
| C(9)-Ru(1)-I(1)-Ru(2) | -61.66(11) |
| C(10)-Ru(1)-I(1)-Ru(2) | -117.00(7) |
| C(11)-Ru(1)-I(1)-Ru(2) | -100.23(5) |
| C(8)-Ru(1)-I(1)-Ru(2) | -37.90(6) |
| C(12)-Ru(1)-I(1)-Ru(2) | -63.23(5) |
| C(6)-Ru(2)-I(1)-Ru(1) | -97.35(5) |
| C(7)-Ru(2)-I(1)-Ru(1) | -4.98(4) |
| C(3)-Ru(2)-I(1)-Ru(1) | 121.62(10) |
| C(4)-Ru(2)-I(1)-Ru(1) | 169.94(5) |
| C(5)-Ru(2)-I(1)-Ru(1) | 153.73(4) |
| C(1)-Ru(2)-I(1)-Ru(1) | 116.37(4) |
| C(2)-Ru(2)-I(1)-Ru(1) | 93.57(5) |

# STRUCTURE TABLES PERTAINING TO CHAPTER 3

## Cyclopentadienyl ruthenium(II) ethylamine complex - $[\eta^5\text{-}C_5H_5Ru(CO)_2CH_2NH_2CH_3]BF_4$




ORTEP diagram

**Table B13:** Crystal data and structure refinement for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2CH_3]BF_4$

| | | |
|---|---|---|
| Empirical formula | C9 H12 B F4 N O2 Ru | |
| Formula weight | 354.08 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | Pbca | |
| Unit cell dimensions | a = 14.6686(5) Å | α= 90°. |
| | b = 11.3131(4) Å | β= 90°. |
| | c = 14.9801(6) Å | γ = 90°. |
| Volume | 2485.91(16) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.892 $Mg/m^3$ | |
| Absorption coefficient | 1.303 $mm^{-1}$ | |
| F(000) | 1392 | |
| Crystal size | 0.23 x 0.15 x 0.13 $mm^3$ | |
| Theta range for data collection | 2.65 to 28.40°. | |
| Index ranges | -19<=h<=19, -15<=k<=14, -19<=l<=19 | |
| Reflections collected | 63059 | |
| Independent reflections | 3103 [R(int) = 0.0190] | |
| Completeness to theta = 28.40° | 99.6 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.8489 and 0.7537 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3103 / 0 / 164 | |
| Goodness-of-fit on $F^2$ | 1.076 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0148, wR2 = 0.0390 | |
| R indices (all data) | R1 = 0.0164, wR2 = 0.0409 | |
| Largest diff. peak and hole | 0.438 and -0.409 $e.Å^{-3}$ | |

**Table B14:** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2CH_3]BF_4$. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 5755(1) | 4314(1) | 3395(1) | 21(1) |
| C(2) | 6478(1) | 4409(1) | 4013(1) | 22(1) |
| C(3) | 6317(1) | 5435(1) | 4555(1) | 22(1) |
| C(4) | 5482(1) | 5944(1) | 4267(1) | 20(1) |
| C(5) | 5134(1) | 5265(1) | 3542(1) | 19(1) |
| C(6) | 7760(1) | 6301(1) | 3173(1) | 17(1) |
| C(7) | 6263(1) | 7681(1) | 2982(1) | 17(1) |
| C(8) | 5734(1) | 6096(1) | 1196(1) | 21(1) |
| C(9) | 5940(1) | 5990(1) | 204(1) | 23(1) |
| B(1) | 8322(1) | 7742(1) | 979(1) | 19(1) |
| F(1) | 9123(1) | 8172(1) | 1350(1) | 31(1) |
| F(2) | 8279(1) | 8027(1) | 89(1) | 44(1) |
| F(3) | 7584(1) | 8247(1) | 1427(1) | 39(1) |
| F(4) | 8281(1) | 6514(1) | 1084(1) | 22(1) |
| N(2) | 6529(1) | 5740(1) | 1749(1) | 15(1) |
| O(1) | 8524(1) | 6445(1) | 3205(1) | 24(1) |
| O(2) | 6123(1) | 8667(1) | 2925(1) | 25(1) |
| Ru(1) | 6475(1) | 6045(1) | 3157(1) | 12(1) |

**Table B15:** Bond lengths [Å] and angles [°] for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2CH_3]BF_4$.

| | |
|---|---|
| C(1)-C(2) | 1.4117(19) |
| C(1)-C(5) | 1.4268(18) |
| C(1)-Ru(1) | 2.2540(12) |
| C(1)-H(1) | 0.9999 |
| C(2)-C(3) | 1.436(2) |
| C(2)-Ru(1) | 2.2517(13) |
| C(2)-H(2) | 1.0001 |
| C(3)-C(4) | 1.421(2) |
| C(3)-Ru(1) | 2.2174(13) |
| C(3)-H(3) | 1.0001 |
| C(4)-C(5) | 1.4246(18) |
| C(4)-Ru(1) | 2.2144(13) |
| C(4)-H(4) | 1.0000 |
| C(5)-Ru(1) | 2.2315(12) |
| C(5)-H(5) | 1.0000 |
| C(6)-O(1) | 1.1342(17) |
| C(6)-Ru(1) | 1.9068(14) |
| C(7)-O(2) | 1.1368(16) |
| C(7)-Ru(1) | 1.8950(13) |
| C(8)-N(2) | 1.4846(16) |
| C(8)-C(9) | 1.5222(19) |
| C(8)-H(8A) | 0.9900 |
| C(8)-H(8B) | 0.9900 |
| C(9)-H(9A) | 0.9800 |
| C(9)-H(9B) | 0.9800 |
| C(9)-H(9C) | 0.9800 |
| B(1)-F(2) | 1.3721(17) |
| B(1)-F(1) | 1.3875(17) |
| B(1)-F(3) | 1.3961(17) |
| B(1)-F(4) | 1.3990(16) |
| N(2)-Ru(1) | 2.1388(10) |
| N(2)-H(2A) | 0.9199 |
| N(2)-H(2B) | 0.9199 |
| | |
| C(2)-C(1)-C(5) | 108.70(12) |
| C(2)-C(1)-Ru(1) | 71.65(7) |

| | |
|---|---|
| C(5)-C(1)-Ru(1) | 70.60(7) |
| C(2)-C(1)-H(1) | 125.6 |
| C(5)-C(1)-H(1) | 125.6 |
| Ru(1)-C(1)-H(1) | 125.6 |
| C(1)-C(2)-C(3) | 108.00(12) |
| C(1)-C(2)-Ru(1) | 71.83(7) |
| C(3)-C(2)-Ru(1) | 69.96(7) |
| C(1)-C(2)-H(2) | 126.0 |
| C(3)-C(2)-H(2) | 126.0 |
| Ru(1)-C(2)-H(2) | 126.0 |
| C(4)-C(3)-C(2) | 107.30(12) |
| C(4)-C(3)-Ru(1) | 71.19(7) |
| C(2)-C(3)-Ru(1) | 72.56(7) |
| C(4)-C(3)-H(3) | 126.2 |
| C(2)-C(3)-H(3) | 126.2 |
| Ru(1)-C(3)-H(3) | 126.2 |
| C(3)-C(4)-C(5) | 108.77(12) |
| C(3)-C(4)-Ru(1) | 71.42(7) |
| C(5)-C(4)-Ru(1) | 71.97(7) |
| C(3)-C(4)-H(4) | 125.6 |
| C(5)-C(4)-H(4) | 125.6 |
| Ru(1)-C(4)-H(4) | 125.6 |
| C(4)-C(5)-C(1) | 107.20(11) |
| C(4)-C(5)-Ru(1) | 70.66(7) |
| C(1)-C(5)-Ru(1) | 72.31(7) |
| C(4)-C(5)-H(5) | 126.3 |
| C(1)-C(5)-H(5) | 126.3 |
| Ru(1)-C(5)-H(5) | 126.3 |
| O(1)-C(6)-Ru(1) | 178.26(11) |
| O(2)-C(7)-Ru(1) | 176.22(12) |
| N(2)-C(8)-C(9) | 111.59(11) |
| N(2)-C(8)-H(8A) | 109.3 |
| C(9)-C(8)-H(8A) | 109.3 |
| N(2)-C(8)-H(8B) | 109.3 |
| C(9)-C(8)-H(8B) | 109.3 |
| H(8A)-C(8)-H(8B) | 108.0 |
| C(8)-C(9)-H(9A) | 109.5 |
| C(8)-C(9)-H(9B) | 109.5 |

| | |
|---|---|
| H(9A)-C(9)-H(9B) | 109.5 |
| C(8)-C(9)-H(9C) | 109.5 |
| H(9A)-C(9)-H(9C) | 109.5 |
| H(9B)-C(9)-H(9C) | 109.5 |
| F(2)-B(1)-F(1) | 110.22(12) |
| F(2)-B(1)-F(3) | 109.60(12) |
| F(1)-B(1)-F(3) | 108.66(11) |
| F(2)-B(1)-F(4) | 109.91(11) |
| F(1)-B(1)-F(4) | 109.82(11) |
| F(3)-B(1)-F(4) | 108.59(11) |
| C(8)-N(2)-Ru(1) | 118.53(8) |
| C(8)-N(2)-H(2A) | 107.7 |
| Ru(1)-N(2)-H(2A) | 107.7 |
| C(8)-N(2)-H(2B) | 107.7 |
| Ru(1)-N(2)-H(2B) | 107.7 |
| H(2A)-N(2)-H(2B) | 107.1 |
| C(7)-Ru(1)-C(6) | 90.89(6) |
| C(7)-Ru(1)-N(2) | 91.54(5) |
| C(6)-Ru(1)-N(2) | 90.03(4) |
| C(7)-Ru(1)-C(4) | 92.67(5) |
| C(6)-Ru(1)-C(4) | 130.46(5) |
| N(2)-Ru(1)-C(4) | 139.16(5) |
| C(7)-Ru(1)-C(3) | 114.68(5) |
| C(6)-Ru(1)-C(3) | 97.99(5) |
| N(2)-Ru(1)-C(3) | 152.28(5) |
| C(4)-Ru(1)-C(3) | 37.40(5) |
| C(7)-Ru(1)-C(5) | 106.10(5) |
| C(6)-Ru(1)-C(5) | 158.12(5) |
| N(2)-Ru(1)-C(5) | 102.91(4) |
| C(4)-Ru(1)-C(5) | 37.38(5) |
| C(3)-Ru(1)-C(5) | 62.65(5) |
| C(7)-Ru(1)-C(2) | 151.88(5) |
| C(6)-Ru(1)-C(2) | 96.66(5) |
| N(2)-Ru(1)-C(2) | 115.41(5) |
| C(4)-Ru(1)-C(2) | 62.02(5) |
| C(3)-Ru(1)-C(2) | 37.48(5) |
| C(5)-Ru(1)-C(2) | 61.93(5) |
| C(7)-Ru(1)-C(1) | 142.54(5) |

| | |
|---|---|
| C(6)-Ru(1)-C(1) | 126.39(5) |
| N(2)-Ru(1)-C(1) | 91.90(5) |
| C(4)-Ru(1)-C(1) | 61.81(5) |
| C(3)-Ru(1)-C(1) | 62.03(5) |
| C(5)-Ru(1)-C(1) | 37.09(5) |
| C(2)-Ru(1)-C(1) | 36.52(5) |

**Table B16:** Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2CH_3]BF_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 24(1) | 15(1) | 22(1) | 2(1) | 4(1) | -5(1) |
| C(2) | 24(1) | 19(1) | 24(1) | 9(1) | 2(1) | 0(1) |
| C(3) | 26(1) | 26(1) | 14(1) | 5(1) | 0(1) | -5(1) |
| C(4) | 23(1) | 21(1) | 16(1) | 1(1) | 7(1) | -3(1) |
| C(5) | 16(1) | 22(1) | 19(1) | 2(1) | 3(1) | -3(1) |
| C(6) | 20(1) | 18(1) | 14(1) | -1(1) | 0(1) | 1(1) |
| C(7) | 18(1) | 19(1) | 15(1) | 0(1) | 2(1) | 0(1) |
| C(8) | 19(1) | 27(1) | 17(1) | 0(1) | -4(1) | 3(1) |
| C(9) | 27(1) | 26(1) | 16(1) | 2(1) | -4(1) | -1(1) |
| B(1) | 21(1) | 17(1) | 18(1) | -1(1) | 1(1) | -1(1) |
| F(1) | 25(1) | 28(1) | 39(1) | -5(1) | -5(1) | -7(1) |
| F(2) | 80(1) | 32(1) | 20(1) | 4(1) | -9(1) | -6(1) |
| F(3) | 29(1) | 26(1) | 62(1) | -5(1) | 17(1) | 5(1) |
| F(4) | 21(1) | 17(1) | 29(1) | 0(1) | 2(1) | -1(1) |
| N(2) | 16(1) | 17(1) | 13(1) | 0(1) | 0(1) | 0(1) |
| O(1) | 16(1) | 31(1) | 24(1) | -3(1) | -1(1) | -2(1) |
| O(2) | 31(1) | 17(1) | 27(1) | 1(1) | 3(1) | 3(1) |
| Ru(1) | 12(1) | 12(1) | 12(1) | 0(1) | 0(1) | 0(1) |

**Table B17:** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for [$\eta^5$-$C_5H_5Ru(CO)_2NH_2CH_2CH_3]BF_4$.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 5677 | 3668 | 2946 | 25 |
| H(2) | 6995 | 3841 | 4081 | 26 |
| H(3) | 6690 | 5695 | 5078 | 26 |
| H(4) | 5169 | 6633 | 4552 | 24 |
| H(5) | 4539 | 5391 | 3230 | 23 |
| H(8A) | 5568 | 6923 | 1337 | 25 |
| H(8B) | 5206 | 5588 | 1346 | 25 |
| H(9A) | 6128 | 5179 | 67 | 34 |
| H(9B) | 6432 | 6537 | 45 | 34 |
| H(9C) | 5392 | 6186 | -140 | 34 |
| H(2A) | 6623 | 4945 | 1662 | 18 |
| H(2B) | 7033 | 6128 | 1531 | 18 |

**Table B18:** Torsion angles [°] for [$\eta^5$-$C_5H_5Ru(CO)_2NH_2CH_2CH_3]BF_4$.

| | |
|---|---|
| C(5)-C(1)-C(2)-C(3) | -0.27(15) |
| Ru(1)-C(1)-C(2)-C(3) | 60.93(9) |
| C(5)-C(1)-C(2)-Ru(1) | -61.20(9) |
| C(1)-C(2)-C(3)-C(4) | 1.01(15) |
| Ru(1)-C(2)-C(3)-C(4) | 63.13(9) |
| C(1)-C(2)-C(3)-Ru(1) | -62.12(9) |
| C(2)-C(3)-C(4)-C(5) | -1.37(14) |
| Ru(1)-C(3)-C(4)-C(5) | 62.66(9) |
| C(2)-C(3)-C(4)-Ru(1) | -64.04(9) |
| C(3)-C(4)-C(5)-C(1) | 1.21(14) |
| Ru(1)-C(4)-C(5)-C(1) | 63.53(9) |
| C(3)-C(4)-C(5)-Ru(1) | -62.31(9) |
| C(2)-C(1)-C(5)-C(4) | -0.58(14) |
| Ru(1)-C(1)-C(5)-C(4) | -62.44(8) |
| C(2)-C(1)-C(5)-Ru(1) | 61.87(9) |
| C(9)-C(8)-N(2)-Ru(1) | 171.40(8) |

| | |
|---|---|
| O(2)-C(7)-Ru(1)-C(6) | -102.9(19) |
| O(2)-C(7)-Ru(1)-N(2) | 167.1(19) |
| O(2)-C(7)-Ru(1)-C(4) | 27.7(19) |
| O(2)-C(7)-Ru(1)-C(3) | -3.7(19) |
| O(2)-C(7)-Ru(1)-C(5) | 63.2(19) |
| O(2)-C(7)-Ru(1)-C(2) | 3.1(19) |
| O(2)-C(7)-Ru(1)-C(1) | 71.9(19) |
| O(1)-C(6)-Ru(1)-C(7) | 114(4) |
| O(1)-C(6)-Ru(1)-N(2) | -154(4) |
| O(1)-C(6)-Ru(1)-C(4) | 20(4) |
| O(1)-C(6)-Ru(1)-C(3) | -1(4) |
| O(1)-C(6)-Ru(1)-C(5) | -27(4) |
| O(1)-C(6)-Ru(1)-C(2) | -38(4) |
| O(1)-C(6)-Ru(1)-C(1) | -62(4) |
| C(8)-N(2)-Ru(1)-C(7) | -56.63(10) |
| C(8)-N(2)-Ru(1)-C(6) | -147.53(10) |
| C(8)-N(2)-Ru(1)-C(4) | 39.25(13) |
| C(8)-N(2)-Ru(1)-C(3) | 105.03(13) |
| C(8)-N(2)-Ru(1)-C(5) | 50.27(10) |
| C(8)-N(2)-Ru(1)-C(2) | 115.08(10) |
| C(8)-N(2)-Ru(1)-C(1) | 86.06(10) |
| C(3)-C(4)-Ru(1)-C(7) | -128.85(8) |
| C(5)-C(4)-Ru(1)-C(7) | 113.34(8) |
| C(3)-C(4)-Ru(1)-C(6) | -35.40(11) |
| C(5)-C(4)-Ru(1)-C(6) | -153.21(8) |
| C(3)-C(4)-Ru(1)-N(2) | 135.69(9) |
| C(5)-C(4)-Ru(1)-N(2) | 17.88(11) |
| C(5)-C(4)-Ru(1)-C(3) | -117.81(11) |
| C(3)-C(4)-Ru(1)-C(5) | 117.81(11) |
| C(3)-C(4)-Ru(1)-C(2) | 38.31(8) |
| C(5)-C(4)-Ru(1)-C(2) | -79.50(8) |
| C(3)-C(4)-Ru(1)-C(1) | 79.92(8) |
| C(5)-C(4)-Ru(1)-C(1) | -37.89(7) |
| C(4)-C(3)-Ru(1)-C(7) | 58.89(9) |
| C(2)-C(3)-Ru(1)-C(7) | 174.76(8) |
| C(4)-C(3)-Ru(1)-C(6) | 153.58(8) |
| C(2)-C(3)-Ru(1)-C(6) | -90.55(8) |
| C(4)-C(3)-Ru(1)-N(2) | -100.87(11) |

| | |
|---|---|
| C(2)-C(3)-Ru(1)-N(2) | 15.01(14) |
| C(2)-C(3)-Ru(1)-C(4) | 115.87(11) |
| C(4)-C(3)-Ru(1)-C(5) | -37.19(7) |
| C(2)-C(3)-Ru(1)-C(5) | 78.68(8) |
| C(4)-C(3)-Ru(1)-C(2) | -115.87(11) |
| C(4)-C(3)-Ru(1)-C(1) | -79.28(8) |
| C(2)-C(3)-Ru(1)-C(1) | 36.60(8) |
| C(4)-C(5)-Ru(1)-C(7) | -72.67(8) |
| C(1)-C(5)-Ru(1)-C(7) | 171.17(8) |
| C(4)-C(5)-Ru(1)-C(6) | 66.98(16) |
| C(1)-C(5)-Ru(1)-C(6) | -49.18(16) |
| C(4)-C(5)-Ru(1)-N(2) | -168.11(8) |
| C(1)-C(5)-Ru(1)-N(2) | 75.72(8) |
| C(1)-C(5)-Ru(1)-C(4) | -116.16(11) |
| C(4)-C(5)-Ru(1)-C(3) | 37.21(8) |
| C(1)-C(5)-Ru(1)-C(3) | -78.95(8) |
| C(4)-C(5)-Ru(1)-C(2) | 79.76(8) |
| C(1)-C(5)-Ru(1)-C(2) | -36.41(8) |
| C(4)-C(5)-Ru(1)-C(1) | 116.16(11) |
| C(1)-C(2)-Ru(1)-C(7) | 107.64(12) |
| C(3)-C(2)-Ru(1)-C(7) | -10.14(15) |
| C(1)-C(2)-Ru(1)-C(6) | -147.78(8) |
| C(3)-C(2)-Ru(1)-C(6) | 94.45(8) |
| C(1)-C(2)-Ru(1)-N(2) | -54.57(9) |
| C(3)-C(2)-Ru(1)-N(2) | -172.34(7) |
| C(1)-C(2)-Ru(1)-C(4) | 79.54(8) |
| C(3)-C(2)-Ru(1)-C(4) | -38.23(8) |
| C(1)-C(2)-Ru(1)-C(3) | 117.77(11) |
| C(1)-C(2)-Ru(1)-C(5) | 36.98(8) |
| C(3)-C(2)-Ru(1)-C(5) | -80.79(8) |
| C(3)-C(2)-Ru(1)-C(1) | -117.77(11) |
| C(2)-C(1)-Ru(1)-C(7) | -132.39(9) |
| C(5)-C(1)-Ru(1)-C(7) | -14.03(12) |
| C(2)-C(1)-Ru(1)-C(6) | 41.13(10) |
| C(5)-C(1)-Ru(1)-C(6) | 159.49(7) |
| C(2)-C(1)-Ru(1)-N(2) | 132.58(8) |
| C(5)-C(1)-Ru(1)-N(2) | -109.06(8) |
| C(2)-C(1)-Ru(1)-C(4) | -80.17(9) |

| | |
|---|---|
| C(5)-C(1)-Ru(1)-C(4) | 38.18(8) |
| C(2)-C(1)-Ru(1)-C(3) | -37.56(8) |
| C(5)-C(1)-Ru(1)-C(3) | 80.80(8) |
| C(2)-C(1)-Ru(1)-C(5) | -118.36(11) |
| C(5)-C(1)-Ru(1)-C(2) | 118.36(11) |

**Cyclopentadienyl ruthenium(II) propylamine complex - $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_2CH_3]BF_4$**

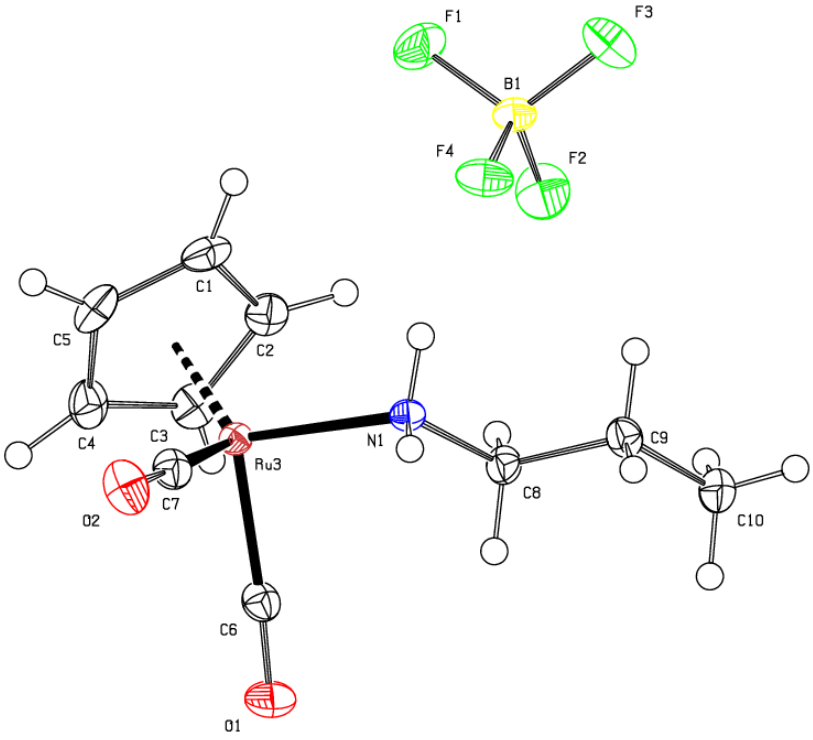


**Table B19:** Crystal data and structure refinement for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_2CH_3]BF_4$

| | | |
|---|---|---|
| Empirical formula | C10 H14 B F4 N O2 Ru | |
| Formula weight | 368.10 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P21/c | |
| Unit cell dimensions | a = 10.4412(2) Å | α= 90°. |
| | b = 7.69910(10) Å | β= 97.7450(10)°. |
| | c = 16.8002(3) Å | γ = 90°. |
| Volume | 1338.21(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.827 $Mg/m^3$ | |
| Absorption coefficient | 1.214 $mm^{-1}$ | |
| F(000) | 728 | |
| Crystal size | 0.47 x 0.26 x 0.15 $mm^3$ | |
| Theta range for data collection | 1.97 to 28.34°. | |
| Index ranges | -13<=h<=13, -10<=k<=10, -22<=l<=21 | |
| Reflections collected | 28712 | |
| Independent reflections | 3325 [R(int) = 0.0203] | |
| Completeness to theta = 28.34° | 99.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.8389 and 0.5992 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3325 / 0 / 173 | |
| Goodness-of-fit on $F^2$ | 1.156 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0161, wR2 = 0.0442 | |
| R indices (all data) | R1 = 0.0172, wR2 = 0.0456 | |
| Largest diff. peak and hole | 0.363 and -0.699 $e.Å^{-3}$ | |

**Table B20:** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_2CH_3]BF_4$ U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 7015(1) | 2743(2) | 6064(1) | 26(1) |
| C(2) | 8243(1) | 2762(2) | 6568(1) | 23(1) |
| C(3) | 9122(1) | 3702(2) | 6167(1) | 24(1) |
| C(4) | 8453(2) | 4287(2) | 5414(1) | 26(1) |
| C(5) | 7167(2) | 3659(2) | 5353(1) | 28(1) |
| C(6) | 8631(1) | 7397(2) | 6699(1) | 20(1) |
| C(7) | 6247(1) | 7080(2) | 5907(1) | 21(1) |
| C(8) | 7716(1) | 5568(2) | 8230(1) | 19(1) |
| C(9) | 7143(1) | 5442(2) | 9007(1) | 20(1) |
| C(10) | 8220(2) | 5431(2) | 9719(1) | 26(1) |
| B(1) | 3361(2) | -386(2) | 1934(1) | 19(1) |
| F(1) | 3454(1) | 638(1) | 2618(1) | 37(1) |
| F(2) | 2074(1) | -661(1) | 1637(1) | 37(1) |
| F(3) | 3991(1) | 429(1) | 1359(1) | 36(1) |
| F(4) | 3966(1) | -1973(1) | 2135(1) | 29(1) |
| N(1) | 6740(1) | 5563(1) | 7501(1) | 15(1) |
| O(1) | 9343(1) | 8503(2) | 6848(1) | 29(1) |
| O(2) | 5523(1) | 8005(2) | 5567(1) | 30(1) |
| Ru(3) | 7517(1) | 5502(1) | 6386(1) | 14(1) |

**Table B21:** Bond lengths [Å] and angles [°] for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_2CH_3]BF_4$

| | |
|---|---|
| C(1)-C(5) | 1.414(2) |
| C(1)-C(2) | 1.439(2) |
| C(1)-Ru(3) | 2.2367(14) |
| C(1)-H(1) | 1.0000 |
| C(2)-C(3) | 1.410(2) |
| C(2)-Ru(3) | 2.2481(14) |
| C(2)-H(2) | 1.0000 |
| C(3)-C(4) | 1.433(2) |
| C(3)-Ru(3) | 2.2427(13) |

| | |
|---|---|
| C(3)-H(3) | 1.0000 |
| C(4)-C(5) | 1.418(2) |
| C(4)-Ru(3) | 2.2196(14) |
| C(4)-H(4) | 1.0000 |
| C(5)-Ru(3) | 2.2338(14) |
| C(5)-H(5) | 1.0000 |
| C(6)-O(1) | 1.1361(17) |
| C(6)-Ru(3) | 1.8953(14) |
| C(7)-O(2) | 1.1351(17) |
| C(7)-Ru(3) | 1.8965(14) |
| C(8)-N(1) | 1.4835(17) |
| C(8)-C(9) | 1.511(2) |
| C(8)-H(8A) | 0.9900 |
| C(8)-H(8B) | 0.9900 |
| C(9)-C(10) | 1.527(2) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-H(10A) | 0.9800 |
| C(10)-H(10B) | 0.9800 |
| C(10)-H(10C) | 0.9800 |
| B(1)-F(2) | 1.3855(17) |
| B(1)-F(1) | 1.3868(18) |
| B(1)-F(3) | 1.3893(18) |
| B(1)-F(4) | 1.3963(16) |
| N(1)-Ru(3) | 2.1402(11) |
| N(1)-H(1A) | 0.9200 |
| N(1)-H(1B) | 0.9200 |

| | |
|---|---|
| C(5)-C(1)-C(2) | 107.44(13) |
| C(5)-C(1)-Ru(3) | 71.45(8) |
| C(2)-C(1)-Ru(3) | 71.71(7) |
| C(5)-C(1)-H(1) | 126.2 |
| C(2)-C(1)-H(1) | 126.2 |
| Ru(3)-C(1)-H(1) | 126.2 |
| C(3)-C(2)-C(1) | 108.04(13) |
| C(3)-C(2)-Ru(3) | 71.50(8) |
| C(1)-C(2)-Ru(3) | 70.85(8) |
| C(3)-C(2)-H(2) | 125.9 |

| | |
|---|---|
| C(1)-C(2)-H(2) | 125.9 |
| Ru(3)-C(2)-H(2) | 125.9 |
| C(2)-C(3)-C(4) | 108.19(12) |
| C(2)-C(3)-Ru(3) | 71.92(8) |
| C(4)-C(3)-Ru(3) | 70.39(8) |
| C(2)-C(3)-H(3) | 125.9 |
| C(4)-C(3)-H(3) | 125.9 |
| Ru(3)-C(3)-H(3) | 125.9 |
| C(5)-C(4)-C(3) | 107.49(13) |
| C(5)-C(4)-Ru(3) | 71.97(8) |
| C(3)-C(4)-Ru(3) | 72.14(8) |
| C(5)-C(4)-H(4) | 126.1 |
| C(3)-C(4)-H(4) | 126.1 |
| Ru(3)-C(4)-H(4) | 126.1 |
| C(1)-C(5)-C(4) | 108.80(13) |
| C(1)-C(5)-Ru(3) | 71.68(8) |
| C(4)-C(5)-Ru(3) | 70.89(8) |
| C(1)-C(5)-H(5) | 125.6 |
| C(4)-C(5)-H(5) | 125.6 |
| Ru(3)-C(5)-H(5) | 125.6 |
| O(1)-C(6)-Ru(3) | 175.64(12) |
| O(2)-C(7)-Ru(3) | 174.76(12) |
| N(1)-C(8)-C(9) | 113.93(12) |
| N(1)-C(8)-H(8A) | 108.8 |
| C(9)-C(8)-H(8A) | 108.8 |
| N(1)-C(8)-H(8B) | 108.8 |
| C(9)-C(8)-H(8B) | 108.8 |
| H(8A)-C(8)-H(8B) | 107.7 |
| C(8)-C(9)-C(10) | 109.98(13) |
| C(8)-C(9)-H(9A) | 109.7 |
| C(10)-C(9)-H(9A) | 109.7 |
| C(8)-C(9)-H(9B) | 109.7 |
| C(10)-C(9)-H(9B) | 109.7 |
| H(9A)-C(9)-H(9B) | 108.2 |
| C(9)-C(10)-H(10A) | 109.5 |
| C(9)-C(10)-H(10B) | 109.5 |
| H(10A)-C(10)-H(10B) | 109.5 |
| C(9)-C(10)-H(10C) | 109.5 |

| | |
|---|---|
| H(10A)-C(10)-H(10C) | 109.5 |
| H(10B)-C(10)-H(10C) | 109.5 |
| F(2)-B(1)-F(1) | 109.98(12) |
| F(2)-B(1)-F(3) | 110.26(13) |
| F(1)-B(1)-F(3) | 109.49(12) |
| F(2)-B(1)-F(4) | 109.75(11) |
| F(1)-B(1)-F(4) | 108.52(12) |
| F(3)-B(1)-F(4) | 108.81(12) |
| C(8)-N(1)-Ru(3) | 115.06(8) |
| C(8)-N(1)-H(1A) | 108.5 |
| Ru(3)-N(1)-H(1A) | 108.5 |
| C(8)-N(1)-H(1B) | 108.5 |
| Ru(3)-N(1)-H(1B) | 108.5 |
| H(1A)-N(1)-H(1B) | 107.5 |
| C(6)-Ru(3)-C(7) | 89.56(6) |
| C(6)-Ru(3)-N(1) | 91.78(5) |
| C(7)-Ru(3)-N(1) | 91.79(5) |
| C(6)-Ru(3)-C(4) | 102.34(6) |
| C(7)-Ru(3)-C(4) | 108.05(6) |
| N(1)-Ru(3)-C(4) | 155.49(5) |
| C(6)-Ru(3)-C(5) | 137.27(6) |
| C(7)-Ru(3)-C(5) | 92.61(6) |
| N(1)-Ru(3)-C(5) | 130.74(5) |
| C(4)-Ru(3)-C(5) | 37.14(6) |
| C(6)-Ru(3)-C(1) | 155.96(6) |
| C(7)-Ru(3)-C(1) | 112.20(6) |
| N(1)-Ru(3)-C(1) | 97.40(5) |
| C(4)-Ru(3)-C(1) | 62.23(6) |
| C(5)-Ru(3)-C(1) | 36.88(6) |
| C(6)-Ru(3)-C(3) | 94.42(6) |
| C(7)-Ru(3)-C(3) | 145.26(5) |
| N(1)-Ru(3)-C(3) | 122.48(5) |
| C(4)-Ru(3)-C(3) | 37.47(5) |
| C(5)-Ru(3)-C(3) | 61.82(5) |
| C(1)-Ru(3)-C(3) | 61.95(5) |
| C(6)-Ru(3)-C(2) | 120.10(5) |
| C(7)-Ru(3)-C(2) | 149.62(6) |
| N(1)-Ru(3)-C(2) | 93.56(5) |

| | |
|---|---|
| C(4)-Ru(3)-C(2) | 62.05(5) |
| C(5)-Ru(3)-C(2) | 61.75(5) |
| C(1)-Ru(3)-C(2) | 37.43(5) |
| C(3)-Ru(3)-C(2) | 36.59(5) |

**Table B22:** Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_2CH_3]BF_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 25(1) | 20(1) | 33(1) | -11(1) | 5(1) | -4(1) |
| C(2) | 28(1) | 17(1) | 25(1) | -2(1) | 4(1) | 6(1) |
| C(3) | 19(1) | 25(1) | 28(1) | -4(1) | 5(1) | 6(1) |
| C(4) | 30(1) | 30(1) | 22(1) | -3(1) | 11(1) | 5(1) |
| C(5) | 30(1) | 30(1) | 23(1) | -11(1) | -3(1) | 4(1) |
| C(6) | 16(1) | 24(1) | 21(1) | 2(1) | 4(1) | 0(1) |
| C(7) | 16(1) | 25(1) | 21(1) | 1(1) | 4(1) | -1(1) |
| C(8) | 16(1) | 25(1) | 16(1) | 0(1) | 1(1) | -2(1) |
| C(9) | 22(1) | 20(1) | 19(1) | 1(1) | 6(1) | 2(1) |
| C(10) | 33(1) | 27(1) | 18(1) | 2(1) | 1(1) | -2(1) |
| B(1) | 17(1) | 15(1) | 25(1) | -1(1) | 2(1) | 0(1) |
| F(1) | 51(1) | 23(1) | 35(1) | -11(1) | 5(1) | 0(1) |
| F(2) | 17(1) | 53(1) | 39(1) | 4(1) | -3(1) | -1(1) |
| F(3) | 35(1) | 33(1) | 42(1) | 12(1) | 14(1) | -1(1) |
| F(4) | 28(1) | 14(1) | 45(1) | 1(1) | 4(1) | 2(1) |
| N(1) | 14(1) | 14(1) | 18(1) | -1(1) | 2(1) | -1(1) |
| O(1) | 24(1) | 29(1) | 36(1) | -1(1) | 3(1) | -11(1) |
| O(2) | 22(1) | 37(1) | 30(1) | 10(1) | 3(1) | 8(1) |
| Ru(3) | 11(1) | 16(1) | 15(1) | -1(1) | 1(1) | -1(1) |

**Table B23:** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for [$\eta^5$-$C_5H_5Ru(CO)_2NH_2(CH_2)_2CH_3]BF_4$.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 6221 | 2111 | 6174 | 31 |
| H(2) | 8450 | 2156 | 7096 | 28 |
| H(3) | 10062 | 3875 | 6361 | 29 |
| H(4) | 8846 | 4916 | 4985 | 32 |
| H(5) | 6491 | 3793 | 4875 | 34 |
| H(8A) | 8230 | 6649 | 8236 | 23 |
| H(8B) | 8313 | 4579 | 8199 | 23 |
| H(9A) | 6626 | 4365 | 9010 | 24 |
| H(9B) | 6563 | 6443 | 9054 | 24 |
| H(10A) | 8815 | 4470 | 9658 | 39 |
| H(10B) | 7844 | 5281 | 10218 | 39 |
| H(10C) | 8692 | 6533 | 9737 | 39 |
| H(1A) | 6234 | 6539 | 7509 | 18 |
| H(1B) | 6212 | 4612 | 7523 | 18 |

**Table B24:** Torsion angles [°] for [$\eta^5$-$C_5H_5Ru(CO)_2NH_2(CH_2)_2CH_3]BF_4$

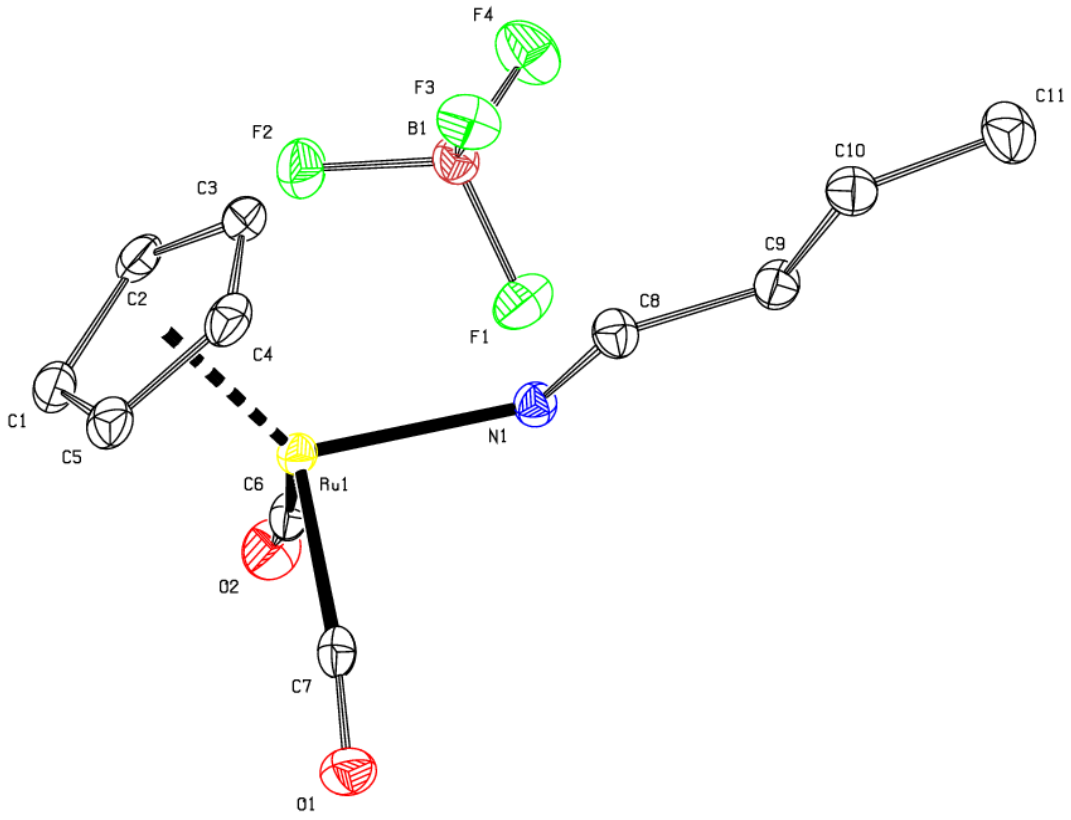
| | |
|---|---|
| C(5)-C(1)-C(2)-C(3) | 0.73(15) |
| Ru(3)-C(1)-C(2)-C(3) | -62.20(9) |
| C(5)-C(1)-C(2)-Ru(3) | 62.93(10) |
| C(1)-C(2)-C(3)-C(4) | 0.40(15) |
| Ru(3)-C(2)-C(3)-C(4) | -61.39(10) |
| C(1)-C(2)-C(3)-Ru(3) | 61.79(9) |
| C(2)-C(3)-C(4)-C(5) | -1.37(16) |
| Ru(3)-C(3)-C(4)-C(5) | -63.74(10) |
| C(2)-C(3)-C(4)-Ru(3) | 62.36(10) |
| C(2)-C(1)-C(5)-C(4) | -1.60(16) |
| Ru(3)-C(1)-C(5)-C(4) | 61.51(10) |
| C(2)-C(1)-C(5)-Ru(3) | -63.11(9) |
| C(3)-C(4)-C(5)-C(1) | 1.84(16) |

| | |
|---|---|
| Ru(3)-C(4)-C(5)-C(1) | -62.00(10) |
| C(3)-C(4)-C(5)-Ru(3) | 63.85(10) |
| N(1)-C(8)-C(9)-C(10) | 179.18(11) |
| C(9)-C(8)-N(1)-Ru(3) | -174.59(8) |
| O(1)-C(6)-Ru(3)-C(7) | -105.3(17) |
| O(1)-C(6)-Ru(3)-N(1) | 162.9(17) |
| O(1)-C(6)-Ru(3)-C(4) | 3.1(17) |
| O(1)-C(6)-Ru(3)-C(5) | -12.0(17) |
| O(1)-C(6)-Ru(3)-C(1) | 50.2(17) |
| O(1)-C(6)-Ru(3)-C(3) | 40.1(17) |
| O(1)-C(6)-Ru(3)-C(2) | 67.7(17) |
| O(2)-C(7)-Ru(3)-C(6) | 94.2(14) |
| O(2)-C(7)-Ru(3)-N(1) | -174.0(14) |
| O(2)-C(7)-Ru(3)-C(4) | -8.6(14) |
| O(2)-C(7)-Ru(3)-C(5) | -43.1(14) |
| O(2)-C(7)-Ru(3)-C(1) | -75.3(14) |
| O(2)-C(7)-Ru(3)-C(3) | -2.9(15) |
| O(2)-C(7)-Ru(3)-C(2) | -73.8(14) |
| C(8)-N(1)-Ru(3)-C(6) | -50.88(9) |
| C(8)-N(1)-Ru(3)-C(7) | -140.49(9) |
| C(8)-N(1)-Ru(3)-C(4) | 74.84(15) |
| C(8)-N(1)-Ru(3)-C(5) | 124.52(9) |
| C(8)-N(1)-Ru(3)-C(1) | 106.85(9) |
| C(8)-N(1)-Ru(3)-C(3) | 45.50(10) |
| C(8)-N(1)-Ru(3)-C(2) | 69.43(9) |
| C(5)-C(4)-Ru(3)-C(6) | -163.06(9) |
| C(3)-C(4)-Ru(3)-C(6) | 81.03(9) |
| C(5)-C(4)-Ru(3)-C(7) | -69.45(10) |
| C(3)-C(4)-Ru(3)-C(7) | 174.64(9) |
| C(5)-C(4)-Ru(3)-N(1) | 73.12(15) |
| C(3)-C(4)-Ru(3)-N(1) | -42.80(17) |
| C(3)-C(4)-Ru(3)-C(5) | -115.91(13) |
| C(5)-C(4)-Ru(3)-C(1) | 36.67(9) |
| C(3)-C(4)-Ru(3)-C(1) | -79.24(9) |
| C(5)-C(4)-Ru(3)-C(3) | 115.91(13) |
| C(5)-C(4)-Ru(3)-C(2) | 79.23(10) |
| C(3)-C(4)-Ru(3)-C(2) | -36.68(8) |
| C(1)-C(5)-Ru(3)-C(6) | 143.10(9) |

| | |
|---|---|
| C(4)-C(5)-Ru(3)-C(6) | 24.81(13) |
| C(1)-C(5)-Ru(3)-C(7) | -124.73(9) |
| C(4)-C(5)-Ru(3)-C(7) | 116.98(9) |
| C(1)-C(5)-Ru(3)-N(1) | -30.11(11) |
| C(4)-C(5)-Ru(3)-N(1) | -148.41(8) |
| C(1)-C(5)-Ru(3)-C(4) | 118.29(13) |
| C(4)-C(5)-Ru(3)-C(1) | -118.29(13) |
| C(1)-C(5)-Ru(3)-C(3) | 79.93(9) |
| C(4)-C(5)-Ru(3)-C(3) | -38.37(9) |
| C(1)-C(5)-Ru(3)-C(2) | 38.19(9) |
| C(4)-C(5)-Ru(3)-C(2) | -80.10(9) |
| C(5)-C(1)-Ru(3)-C(6) | -90.96(16) |
| C(2)-C(1)-Ru(3)-C(6) | 25.39(18) |
| C(5)-C(1)-Ru(3)-C(7) | 62.47(10) |
| C(2)-C(1)-Ru(3)-C(7) | 178.82(8) |
| C(5)-C(1)-Ru(3)-N(1) | 157.46(8) |
| C(2)-C(1)-Ru(3)-N(1) | -86.19(8) |
| C(5)-C(1)-Ru(3)-C(4) | -36.93(9) |
| C(2)-C(1)-Ru(3)-C(4) | 79.42(9) |
| C(2)-C(1)-Ru(3)-C(5) | 116.35(12) |
| C(5)-C(1)-Ru(3)-C(3) | -79.55(9) |
| C(2)-C(1)-Ru(3)-C(3) | 36.80(8) |
| C(5)-C(1)-Ru(3)-C(2) | -116.35(12) |
| C(2)-C(3)-Ru(3)-C(6) | 137.71(9) |
| C(4)-C(3)-Ru(3)-C(6) | -104.58(9) |
| C(2)-C(3)-Ru(3)-C(7) | -126.67(11) |
| C(4)-C(3)-Ru(3)-C(7) | -8.97(14) |
| C(2)-C(3)-Ru(3)-N(1) | 42.77(10) |
| C(4)-C(3)-Ru(3)-N(1) | 160.48(8) |
| C(2)-C(3)-Ru(3)-C(4) | -117.71(12) |
| C(2)-C(3)-Ru(3)-C(5) | -79.68(9) |
| C(4)-C(3)-Ru(3)-C(5) | 38.03(9) |
| C(2)-C(3)-Ru(3)-C(1) | -37.65(8) |
| C(4)-C(3)-Ru(3)-C(1) | 80.06(9) |
| C(4)-C(3)-Ru(3)-C(2) | 117.71(12) |
| C(3)-C(2)-Ru(3)-C(6) | -50.84(10) |
| C(1)-C(2)-Ru(3)-C(6) | -168.35(8) |
| C(3)-C(2)-Ru(3)-C(7) | 115.35(12) |

| | |
|---|---|
| C(1)-C(2)-Ru(3)-C(7) | -2.16(15) |
| C(3)-C(2)-Ru(3)-N(1) | -144.97(8) |
| C(1)-C(2)-Ru(3)-N(1) | 97.52(9) |
| C(3)-C(2)-Ru(3)-C(4) | 37.57(8) |
| C(1)-C(2)-Ru(3)-C(4) | -79.95(9) |
| C(3)-C(2)-Ru(3)-C(5) | 79.89(9) |
| C(1)-C(2)-Ru(3)-C(5) | -37.62(9) |
| C(3)-C(2)-Ru(3)-C(1) | 117.51(12) |
| C(1)-C(2)-Ru(3)-C(3) | -117.51(12) |

## Cyclopentadienyl ruthenium(II) butylamine complex - $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_3CH_3]BF_4$




**ORTEP Diagram**

**Table B25:** Crystal data and structure refinement for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_3CH_3]BF_4$.

| | | |
|---|---|---|
| Empirical formula | C11 H16 B F4 N O2 Ru | |
| Formula weight | 382.13 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P21/c | |
| Unit cell dimensions | a = 9.1329(5) Å | α= 90°. |
| | b = 8.4964(4) Å | β= 112.154(2)°. |
| | c = 19.3325(9) Å | γ = 90°. |
| Volume | 1389.39(12) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.827 $Mg/m^3$ | |
| Absorption coefficient | 1.173 $mm^{-1}$ | |
| F(000) | 760 | |
| Crystal size | 0.36 x 0.25 x 0.21 $mm^3$ | |
| Theta range for data collection | 2.41 to 25.00°. | |
| Index ranges | -10<=h<=10, -10<=k<=10, -22<=l<=19 | |
| Reflections collected | 20134 | |
| Independent reflections | 2417 [R(int) = 0.0377] | |
| Completeness to theta = 25.00° | 98.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7908 and 0.6775 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2417 / 0 / 182 | |
| Goodness-of-fit on $F^2$ | 1.301 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0262, wR2 = 0.0630 | |
| R indices (all data) | R1 = 0.0275, wR2 = 0.0637 | |
| Largest diff. peak and hole | 0.740 and -0.430 $e.Å^{-3}$ | |

**Table B25:** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_3CH_3]BF_4$. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ru(1) | 7132(1) | 7643(1) | 9358(1) | 14(1) |
| O(1) | 6800(3) | 10324(3) | 10323(1) | 24(1) |
| O(2) | 7987(3) | 5237(3) | 10606(1) | 26(1) |
| N(1) | 4689(3) | 6982(3) | 8964(1) | 16(1) |
| C(1) | 9503(4) | 7618(4) | 9297(2) | 20(1) |
| C(2) | 8574(4) | 6411(4) | 8807(2) | 20(1) |
| C(3) | 7290(4) | 7141(4) | 8245(2) | 21(1) |
| C(4) | 7384(4) | 8788(4) | 8368(2) | 21(1) |
| C(5) | 8762(4) | 9085(4) | 9014(2) | 20(1) |
| C(6) | 7592(4) | 6151(4) | 10141(2) | 19(1) |
| C(7) | 6849(4) | 9294(4) | 9956(2) | 17(1) |
| C(8) | 3600(4) | 7716(4) | 8256(2) | 18(1) |
| C(9) | 1961(4) | 6972(4) | 7986(2) | 19(1) |
| C(10) | 909(4) | 7534(4) | 7207(2) | 20(1) |
| C(11) | -686(4) | 6699(5) | 6915(2) | 27(1) |
| F(1) | 5206(2) | 3374(2) | 9419(1) | 28(1) |
| F(2) | 7340(2) | 2668(2) | 9151(1) | 27(1) |
| F(3) | 5297(2) | 4018(2) | 8296(1) | 25(1) |
| F(4) | 4971(2) | 1459(2) | 8553(1) | 31(1) |
| B(1) | 5698(4) | 2862(4) | 8854(2) | 19(1) |

**Table B26:** Bond lengths [Å] and angles [°] for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_3CH_3]BF_4$.

| | |
|---|---|
| Ru(1)-C(7) | 1.896(3) |
| Ru(1)-C(6) | 1.896(3) |
| Ru(1)-N(1) | 2.143(3) |
| Ru(1)-C(1) | 2.212(3) |
| Ru(1)-C(5) | 2.215(3) |
| Ru(1)-C(4) | 2.234(3) |
| Ru(1)-C(2) | 2.241(3) |

| | |
|---|---|
| Ru(1)-C(3) | 2.251(3) |
| O(1)-C(7) | 1.138(4) |
| O(2)-C(6) | 1.139(4) |
| N(1)-C(8) | 1.491(4) |
| N(1)-H(1A) | 0.9200 |
| N(1)-H(1B) | 0.9200 |
| C(1)-C(5) | 1.425(5) |
| C(1)-C(2) | 1.436(5) |
| C(1)-H(1) | 1.0000 |
| C(2)-C(3) | 1.407(5) |
| C(2)-H(2) | 1.0000 |
| C(3)-C(4) | 1.417(5) |
| C(3)-H(3) | 1.0000 |
| C(4)-C(5) | 1.422(5) |
| C(4)-H(4) | 1.0000 |
| C(5)-H(5) | 1.0000 |
| C(8)-C(9) | 1.524(4) |
| C(8)-H(8A) | 0.9900 |
| C(8)-H(8B) | 0.9900 |
| C(9)-C(10) | 1.526(4) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-C(11) | 1.524(5) |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-H(11A) | 0.9800 |
| C(11)-H(11B) | 0.9800 |
| C(11)-H(11C) | 0.9800 |
| F(1)-B(1) | 1.399(4) |
| F(2)-B(1) | 1.399(4) |
| F(3)-B(1) | 1.401(4) |
| F(4)-B(1) | 1.381(4) |

| | |
|---|---|
| C(7)-Ru(1)-C(6) | 92.77(13) |
| C(7)-Ru(1)-N(1) | 92.74(12) |
| C(6)-Ru(1)-N(1) | 89.77(12) |
| C(7)-Ru(1)-C(1) | 113.62(13) |
| C(6)-Ru(1)-C(1) | 96.29(13) |

| | |
|---|---|
| N(1)-Ru(1)-C(1) | 152.51(11) |
| C(7)-Ru(1)-C(5) | 92.02(13) |
| C(6)-Ru(1)-C(5) | 129.65(13) |
| N(1)-Ru(1)-C(5) | 139.97(11) |
| C(1)-Ru(1)-C(5) | 37.57(12) |
| C(7)-Ru(1)-C(4) | 106.35(13) |
| C(6)-Ru(1)-C(4) | 155.70(13) |
| N(1)-Ru(1)-C(4) | 103.83(11) |
| C(1)-Ru(1)-C(4) | 62.60(12) |
| C(5)-Ru(1)-C(4) | 37.28(12) |
| C(7)-Ru(1)-C(2) | 151.03(13) |
| C(6)-Ru(1)-C(2) | 94.27(13) |
| N(1)-Ru(1)-C(2) | 115.34(11) |
| C(1)-Ru(1)-C(2) | 37.62(12) |
| C(5)-Ru(1)-C(2) | 62.21(12) |
| C(4)-Ru(1)-C(2) | 61.80(12) |
| C(7)-Ru(1)-C(3) | 142.69(13) |
| C(6)-Ru(1)-C(3) | 124.17(13) |
| N(1)-Ru(1)-C(3) | 92.50(11) |
| C(1)-Ru(1)-C(3) | 62.00(12) |
| C(5)-Ru(1)-C(3) | 61.66(12) |
| C(4)-Ru(1)-C(3) | 36.82(12) |
| C(2)-Ru(1)-C(3) | 36.49(12) |
| C(8)-N(1)-Ru(1) | 117.48(19) |
| C(8)-N(1)-H(1A) | 108.0 |
| Ru(1)-N(1)-H(1A) | 107.9 |
| C(8)-N(1)-H(1B) | 107.9 |
| Ru(1)-N(1)-H(1B) | 107.9 |
| H(1A)-N(1)-H(1B) | 107.2 |
| C(5)-C(1)-C(2) | 107.1(3) |
| C(5)-C(1)-Ru(1) | 71.29(18) |
| C(2)-C(1)-Ru(1) | 72.27(18) |
| C(5)-C(1)-H(1) | 126.3 |
| C(2)-C(1)-H(1) | 126.3 |
| Ru(1)-C(1)-H(1) | 126.3 |
| C(3)-C(2)-C(1) | 108.0(3) |
| C(3)-C(2)-Ru(1) | 72.15(18) |
| C(1)-C(2)-Ru(1) | 70.11(18) |

| | |
|---|---|
| C(3)-C(2)-H(2) | 126.0 |
| C(1)-C(2)-H(2) | 126.0 |
| Ru(1)-C(2)-H(2) | 126.0 |
| C(2)-C(3)-C(4) | 109.0(3) |
| C(2)-C(3)-Ru(1) | 71.36(18) |
| C(4)-C(3)-Ru(1) | 70.92(18) |
| C(2)-C(3)-H(3) | 125.5 |
| C(4)-C(3)-H(3) | 125.5 |
| Ru(1)-C(3)-H(3) | 125.5 |
| C(3)-C(4)-C(5) | 107.5(3) |
| C(3)-C(4)-Ru(1) | 72.26(19) |
| C(5)-C(4)-Ru(1) | 70.62(18) |
| C(3)-C(4)-H(4) | 126.2 |
| C(5)-C(4)-H(4) | 126.2 |
| Ru(1)-C(4)-H(4) | 126.2 |
| C(4)-C(5)-C(1) | 108.5(3) |
| C(4)-C(5)-Ru(1) | 72.10(18) |
| C(1)-C(5)-Ru(1) | 71.14(18) |
| C(4)-C(5)-H(5) | 125.7 |
| C(1)-C(5)-H(5) | 125.7 |
| Ru(1)-C(5)-H(5) | 125.7 |
| O(2)-C(6)-Ru(1) | 174.2(3) |
| O(1)-C(7)-Ru(1) | 174.4(3) |
| N(1)-C(8)-C(9) | 111.7(3) |
| N(1)-C(8)-H(8A) | 109.3 |
| C(9)-C(8)-H(8A) | 109.3 |
| N(1)-C(8)-H(8B) | 109.3 |
| C(9)-C(8)-H(8B) | 109.3 |
| H(8A)-C(8)-H(8B) | 107.9 |
| C(8)-C(9)-C(10) | 112.3(3) |
| C(8)-C(9)-H(9A) | 109.1 |
| C(10)-C(9)-H(9A) | 109.1 |
| C(8)-C(9)-H(9B) | 109.1 |
| C(10)-C(9)-H(9B) | 109.1 |
| H(9A)-C(9)-H(9B) | 107.9 |
| C(11)-C(10)-C(9) | 112.2(3) |
| C(11)-C(10)-H(10A) | 109.2 |
| C(9)-C(10)-H(10A) | 109.2 |

| | |
|---|---|
| C(11)-C(10)-H(10B) | 109.2 |
| C(9)-C(10)-H(10B) | 109.2 |
| H(10A)-C(10)-H(10B) | 107.9 |
| C(10)-C(11)-H(11A) | 109.5 |
| C(10)-C(11)-H(11B) | 109.5 |
| H(11A)-C(11)-H(11B) | 109.5 |
| C(10)-C(11)-H(11C) | 109.5 |
| H(11A)-C(11)-H(11C) | 109.5 |
| H(11B)-C(11)-H(11C) | 109.5 |
| F(4)-B(1)-F(2) | 110.0(3) |
| F(4)-B(1)-F(1) | 110.6(3) |
| F(2)-B(1)-F(1) | 109.0(3) |
| F(4)-B(1)-F(3) | 109.6(3) |
| F(2)-B(1)-F(3) | 109.1(3) |
| F(1)-B(1)-F(3) | 108.4(3) |

**Table B27:** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for [$\eta^5$-$C_5H_5Ru(CO)_2NH_2(CH_2)_3CH_3]BF_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ru(1) | 13(1) | 15(1) | 14(1) | 0(1) | 5(1) | 2(1) |
| O(1) | 25(1) | 22(1) | 24(1) | -4(1) | 9(1) | 2(1) |
| O(2) | 26(1) | 26(1) | 24(1) | 8(1) | 8(1) | 8(1) |
| N(1) | 15(1) | 15(1) | 18(1) | 0(1) | 6(1) | 1(1) |
| C(1) | 15(2) | 27(2) | 20(2) | 1(1) | 8(1) | 2(1) |
| C(2) | 18(2) | 22(2) | 25(2) | -2(1) | 14(1) | 3(1) |
| C(3) | 16(2) | 31(2) | 18(2) | -4(1) | 9(1) | -3(1) |
| C(4) | 19(2) | 28(2) | 20(2) | 5(1) | 12(1) | 3(1) |
| C(5) | 19(2) | 22(2) | 23(2) | 1(1) | 12(1) | -3(1) |
| C(6) | 12(2) | 22(2) | 23(2) | -4(1) | 7(1) | 1(1) |
| C(7) | 12(2) | 20(2) | 18(2) | 4(1) | 5(1) | 1(1) |
| C(8) | 16(2) | 20(2) | 16(2) | 3(1) | 4(1) | 1(1) |
| C(9) | 17(2) | 22(2) | 19(2) | 2(1) | 7(1) | 2(1) |
| C(10) | 21(2) | 22(2) | 17(2) | 2(1) | 7(1) | 0(1) |
| C(11) | 21(2) | 36(2) | 21(2) | 5(2) | 3(1) | 1(2) |
| F(1) | 30(1) | 32(1) | 27(1) | 1(1) | 16(1) | 6(1) |
| F(2) | 18(1) | 35(1) | 26(1) | 1(1) | 6(1) | 4(1) |
| F(3) | 31(1) | 20(1) | 22(1) | 2(1) | 6(1) | 2(1) |
| F(4) | 31(1) | 18(1) | 36(1) | -2(1) | 4(1) | -1(1) |
| B(1) | 16(2) | 18(2) | 20(2) | -1(1) | 5(2) | 2(2) |

**Table B28:** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for [$\eta^5$-$C_5H_5Ru(CO)_2NH_2(CH_2)_3CH_3]BF_4$.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 4317 | 7213 | 9333 | 19 |
| H(1B) | 4631 | 5907 | 8900 | 19 |
| H(1) | 10534 | 7467 | 9725 | 24 |
| H(2) | 8829 | 5262 | 8842 | 24 |
| H(3) | 6467 | 6590 | 7817 | 25 |
| H(4) | 6661 | 9599 | 8039 | 25 |
| H(5) | 9180 | 10147 | 9216 | 24 |
| H(8A) | 4049 | 7593 | 7866 | 21 |
| H(8B) | 3510 | 8856 | 8338 | 21 |
| H(9A) | 1450 | 7236 | 8341 | 23 |
| H(9B) | 2068 | 5813 | 7980 | 23 |
| H(10A) | 736 | 8682 | 7221 | 24 |
| H(10B) | 1455 | 7343 | 6859 | 24 |
| H(11A) | -1224 | 6870 | 7262 | 41 |
| H(11B) | -523 | 5568 | 6873 | 41 |
| H(11C) | -1336 | 7121 | 6423 | 41 |

**Table B29:** Torsion angles [°] for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_3CH_3]BF_4$.

| | |
|---|---|
| C(7)-Ru(1)-N(1)-C(8) | 92.0(2) |
| C(6)-Ru(1)-N(1)-C(8) | -175.3(2) |
| C(1)-Ru(1)-N(1)-C(8) | -72.0(3) |
| C(5)-Ru(1)-N(1)-C(8) | -4.5(3) |
| C(4)-Ru(1)-N(1)-C(8) | -15.6(2) |
| C(2)-Ru(1)-N(1)-C(8) | -80.7(2) |
| C(3)-Ru(1)-N(1)-C(8) | -51.1(2) |
| C(7)-Ru(1)-C(1)-C(5) | -59.6(2) |
| C(6)-Ru(1)-C(1)-C(5) | -155.4(2) |
| N(1)-Ru(1)-C(1)-C(5) | 102.8(3) |
| C(4)-Ru(1)-C(1)-C(5) | 37.23(19) |
| C(2)-Ru(1)-C(1)-C(5) | 115.7(3) |
| C(3)-Ru(1)-C(1)-C(5) | 79.0(2) |
| C(7)-Ru(1)-C(1)-C(2) | -175.36(19) |
| C(6)-Ru(1)-C(1)-C(2) | 88.8(2) |
| N(1)-Ru(1)-C(1)-C(2) | -12.9(3) |
| C(5)-Ru(1)-C(1)-C(2) | -115.7(3) |
| C(4)-Ru(1)-C(1)-C(2) | -78.5(2) |
| C(3)-Ru(1)-C(1)-C(2) | -36.71(19) |
| C(5)-C(1)-C(2)-C(3) | -0.6(3) |
| Ru(1)-C(1)-C(2)-C(3) | 62.6(2) |
| C(5)-C(1)-C(2)-Ru(1) | -63.2(2) |
| C(7)-Ru(1)-C(2)-C(3) | -108.6(3) |
| C(6)-Ru(1)-C(2)-C(3) | 147.8(2) |
| N(1)-Ru(1)-C(2)-C(3) | 56.0(2) |
| C(1)-Ru(1)-C(2)-C(3) | -117.4(3) |
| C(5)-Ru(1)-C(2)-C(3) | -79.1(2) |
| C(4)-Ru(1)-C(2)-C(3) | -36.6(2) |
| C(7)-Ru(1)-C(2)-C(1) | 8.8(4) |
| C(6)-Ru(1)-C(2)-C(1) | -94.8(2) |
| N(1)-Ru(1)-C(2)-C(1) | 173.46(18) |
| C(5)-Ru(1)-C(2)-C(1) | 38.38(19) |
| C(4)-Ru(1)-C(2)-C(1) | 80.8(2) |
| C(3)-Ru(1)-C(2)-C(1) | 117.4(3) |
| C(1)-C(2)-C(3)-C(4) | 0.0(4) |
| Ru(1)-C(2)-C(3)-C(4) | 61.3(2) |

| | |
|---|---|
| C(1)-C(2)-C(3)-Ru(1) | -61.3(2) |
| C(7)-Ru(1)-C(3)-C(2) | 130.8(2) |
| C(6)-Ru(1)-C(3)-C(2) | -40.0(2) |
| N(1)-Ru(1)-C(3)-C(2) | -131.4(2) |
| C(1)-Ru(1)-C(3)-C(2) | 37.8(2) |
| C(5)-Ru(1)-C(3)-C(2) | 80.7(2) |
| C(4)-Ru(1)-C(3)-C(2) | 118.7(3) |
| C(7)-Ru(1)-C(3)-C(4) | 12.1(3) |
| C(6)-Ru(1)-C(3)-C(4) | -158.7(2) |
| N(1)-Ru(1)-C(3)-C(4) | 109.9(2) |
| C(1)-Ru(1)-C(3)-C(4) | -80.8(2) |
| C(5)-Ru(1)-C(3)-C(4) | -37.99(19) |
| C(2)-Ru(1)-C(3)-C(4) | -118.7(3) |
| C(2)-C(3)-C(4)-C(5) | 0.7(4) |
| Ru(1)-C(3)-C(4)-C(5) | 62.2(2) |
| C(2)-C(3)-C(4)-Ru(1) | -61.5(2) |
| C(7)-Ru(1)-C(4)-C(3) | -172.4(2) |
| C(6)-Ru(1)-C(4)-C(3) | 47.1(4) |
| N(1)-Ru(1)-C(4)-C(3) | -75.3(2) |
| C(1)-Ru(1)-C(4)-C(3) | 79.0(2) |
| C(5)-Ru(1)-C(4)-C(3) | 116.6(3) |
| C(2)-Ru(1)-C(4)-C(3) | 36.30(19) |
| C(7)-Ru(1)-C(4)-C(5) | 71.0(2) |
| C(6)-Ru(1)-C(4)-C(5) | -69.5(4) |
| N(1)-Ru(1)-C(4)-C(5) | 168.14(19) |
| C(1)-Ru(1)-C(4)-C(5) | -37.52(19) |
| C(2)-Ru(1)-C(4)-C(5) | -80.3(2) |
| C(3)-Ru(1)-C(4)-C(5) | -116.6(3) |
| C(3)-C(4)-C(5)-C(1) | -1.0(4) |
| Ru(1)-C(4)-C(5)-C(1) | 62.2(2) |
| C(3)-C(4)-C(5)-Ru(1) | -63.3(2) |
| C(2)-C(1)-C(5)-C(4) | 1.0(4) |
| Ru(1)-C(1)-C(5)-C(4) | -62.8(2) |
| C(2)-C(1)-C(5)-Ru(1) | 63.9(2) |
| C(7)-Ru(1)-C(5)-C(4) | -114.8(2) |
| C(6)-Ru(1)-C(5)-C(4) | 150.0(2) |
| N(1)-Ru(1)-C(5)-C(4) | -18.1(3) |
| C(1)-Ru(1)-C(5)-C(4) | 117.5(3) |

| | |
|---|---|
| C(2)-Ru(1)-C(5)-C(4) | 79.1(2) |
| C(3)-Ru(1)-C(5)-C(4) | 37.51(19) |
| C(7)-Ru(1)-C(5)-C(1) | 127.7(2) |
| C(6)-Ru(1)-C(5)-C(1) | 32.5(3) |
| N(1)-Ru(1)-C(5)-C(1) | -135.6(2) |
| C(4)-Ru(1)-C(5)-C(1) | -117.5(3) |
| C(2)-Ru(1)-C(5)-C(1) | -38.43(19) |
| C(3)-Ru(1)-C(5)-C(1) | -80.0(2) |
| Ru(1)-N(1)-C(8)-C(9) | 172.0(2) |
| N(1)-C(8)-C(9)-C(10) | -171.4(3) |
| C(8)-C(9)-C(10)-C(11) | 175.8(3) |

**Cyclopentadienyl ruthenium(II) pentylamine complex - $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_4CH_3]BF_4$**

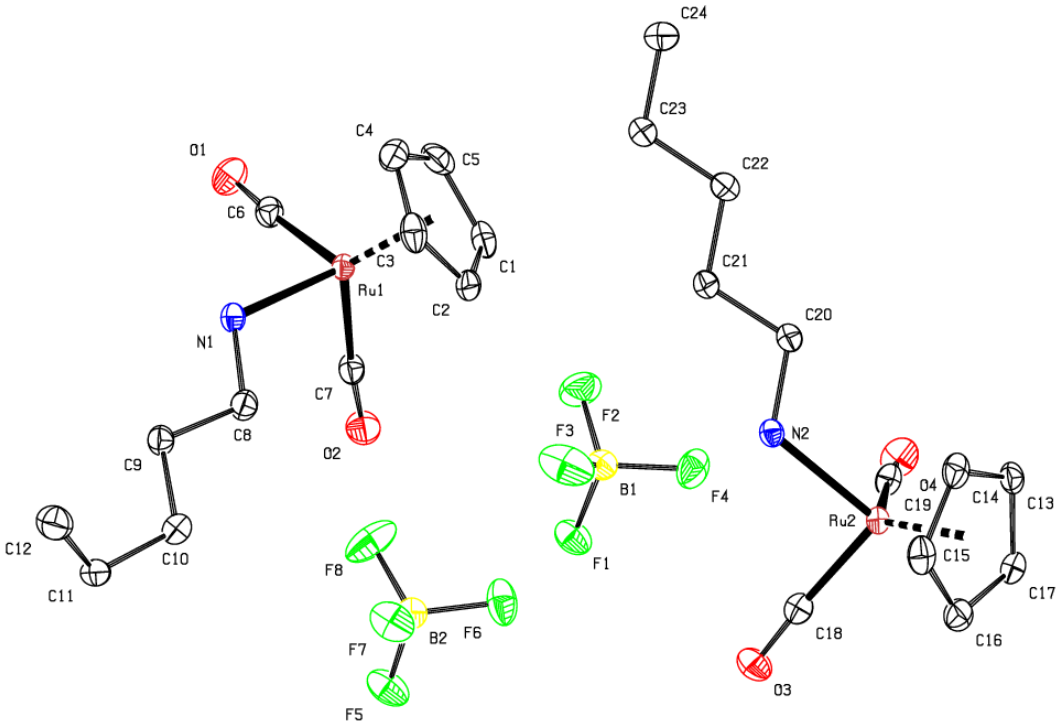


**Table B30:** Crystal data and structure refinement for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_4CH_3]BF_4$.

| | | |
|---|---|---|
| Identification code | 12bo_hbf_ne2b_0m | |
| Empirical formula | C12 H18 B F4 N O2 Ru | |
| Formula weight | 396.15 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P21/c | |
| Unit cell dimensions | a = 14.4432(3) Å | α= 90°. |
| | b = 14.1166(3) Å | β= 115.978(2)°. |
| | c = 17.0859(4) Å | γ = 90°. |
| Volume | 3131.65(12) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.680 $Mg/m^3$ | |
| Absorption coefficient | 1.044 $mm^{-1}$ | |
| F(000) | 1584 | |
| Crystal size | 0.13 x 0.23 x 0.50 $mm^3$ | |
| Theta range for data collection | 1.96 to 28.42°. | |
| Index ranges | -19<=h<=19, -18<=k<=18, -22<=l<=22 | |
| Reflections collected | 52347 | |
| Independent reflections | 7542 [R(int) = 0.0329] | |
| Completeness to theta = 28.42° | 95.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 7542 / 0 / 381 | |
| Goodness-of-fit on $F^2$ | 1.131 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0257, wR2 = 0.0648 | |
| R indices (all data) | R1 = 0.0372, wR2 = 0.0728 | |
| Largest diff. peak and hole | 0.552 and -0.822 $e.Å^{-3}$ | |

**Table B31:** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_4CH_3]BF_4$. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 5371(2) | 801(2) | 2794(2) | 24(1) |
| C(2) | 5723(2) | 1574(2) | 2453(2) | 22(1) |
| C(3) | 5712(2) | 1274(2) | 1661(2) | 25(1) |
| C(4) | 5352(2) | 324(2) | 1498(2) | 29(1) |
| C(5) | 5148(2) | 30(2) | 2203(2) | 29(1) |
| C(6) | 2933(2) | 395(2) | 1069(2) | 21(1) |
| C(7) | 3451(2) | 1978(2) | 2080(2) | 20(1) |
| C(8) | 3720(2) | 3096(2) | 514(2) | 22(1) |
| C(9) | 3184(2) | 3663(2) | -319(2) | 20(1) |
| C(10) | 3457(2) | 4713(2) | -153(2) | 22(1) |
| C(11) | 2906(2) | 5355(2) | -944(2) | 22(1) |
| C(12) | 3184(2) | 5156(2) | -1689(2) | 33(1) |
| C(13) | 10709(2) | 1626(2) | 2545(2) | 21(1) |
| C(14) | 10743(2) | 1390(2) | 1756(2) | 23(1) |
| C(15) | 10405(2) | 433(2) | 1539(2) | 24(1) |
| C(16) | 10175(2) | 76(2) | 2213(2) | 25(1) |
| C(17) | 10343(2) | 811(2) | 2830(2) | 21(1) |
| C(18) | 7949(2) | 430(2) | 1147(2) | 20(1) |
| C(19) | 8428(2) | 2111(2) | 2007(2) | 21(1) |
| C(20) | 8805(2) | 2980(2) | 331(2) | 19(1) |
| C(21) | 8213(2) | 3437(2) | -557(2) | 19(1) |
| C(22) | 8644(2) | 4412(2) | -610(2) | 20(1) |
| C(23) | 8088(2) | 4869(2) | -1505(2) | 23(1) |
| C(24) | 8587(2) | 5787(2) | -1591(2) | 27(1) |
| B(1) | 5605(2) | 2814(2) | 4505(2) | 22(1) |
| B(2) | 10674(2) | 2976(2) | 4531(2) | 20(1) |
| F(1) | 4852(1) | 3396(1) | 4559(1) | 28(1) |
| F(2) | 5241(1) | 1898(1) | 4318(1) | 40(1) |
| F(3) | 5887(2) | 3150(1) | 3880(1) | 48(1) |
| F(4) | 6477(1) | 2816(1) | 5311(1) | 35(1) |
| F(5) | 9972(1) | 3582(1) | 4629(1) | 32(1) |
| F(6) | 11462(1) | 2772(1) | 5355(1) | 35(1) |
| F(7) | 11122(1) | 3406(1) | 4045(1) | 34(1) |

| | | | | |
|---|---|---|---|---|
| F(8) | 10201(1) | 2148(1) | 4142(1) | 45(1) |
| N(1) | 3503(1) | 2064(1) | 388(1) | 17(1) |
| N(2) | 8500(1) | 1973(1) | 335(1) | 16(1) |
| O(1) | 2269(1) | -132(1) | 826(1) | 30(1) |
| O(2) | 3121(1) | 2407(1) | 2459(1) | 29(1) |
| O(3) | 7283(1) | -93(1) | 932(1) | 28(1) |
| O(4) | 8064(2) | 2606(1) | 2318(1) | 31(1) |
| Ru(1) | 4094(1) | 1209(1) | 1545(1) | 15(1) |
| Ru(2) | 9101(1) | 1254(1) | 1565(1) | 15(1) |

**Table 32:** Bond lengths [Å] and angles [°] for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_4CH_3]BF_4$

| | |
|---|---|
| C(1)-C(5) | 1.423(4) |
| C(1)-C(2) | 1.432(3) |
| C(1)-Ru(1) | 2.199(2) |
| C(1)-H(1) | 0.9801 |
| C(2)-C(3) | 1.411(3) |
| C(2)-Ru(1) | 2.238(2) |
| C(2)-H(2) | 0.9799 |
| C(3)-C(4) | 1.421(4) |
| C(3)-Ru(1) | 2.259(2) |
| C(3)-H(3) | 0.9800 |
| C(4)-C(5) | 1.422(4) |
| C(4)-Ru(1) | 2.235(2) |
| C(4)-H(4) | 0.9800 |
| C(5)-Ru(1) | 2.202(2) |
| C(5)-H(5) | 0.9800 |
| C(6)-O(1) | 1.138(3) |
| C(6)-Ru(1) | 1.897(2) |
| C(7)-O(2) | 1.133(3) |
| C(7)-Ru(1) | 1.902(2) |
| C(8)-N(1) | 1.487(3) |
| C(8)-C(9) | 1.515(3) |
| C(8)-H(8A) | 0.9700 |
| C(8)-H(8B) | 0.9700 |

| | |
|---|---|
| C(9)-C(10) | 1.528(3) |
| C(9)-H(9A) | 0.9700 |
| C(9)-H(9B) | 0.9700 |
| C(10)-C(11) | 1.529(3) |
| C(10)-H(10A) | 0.9700 |
| C(10)-H(10B) | 0.9700 |
| C(11)-C(12) | 1.519(3) |
| C(11)-H(11A) | 0.9700 |
| C(11)-H(11B) | 0.9700 |
| C(12)-H(12A) | 0.9600 |
| C(12)-H(12B) | 0.9600 |
| C(12)-H(12C) | 0.9600 |
| C(13)-C(14) | 1.411(3) |
| C(13)-C(17) | 1.438(3) |
| C(13)-Ru(2) | 2.250(2) |
| C(13)-H(13) | 0.9800 |
| C(14)-C(15) | 1.428(3) |
| C(14)-Ru(2) | 2.256(2) |
| C(14)-H(14) | 0.9800 |
| C(15)-C(16) | 1.423(3) |
| C(15)-Ru(2) | 2.229(2) |
| C(15)-H(15) | 0.9800 |
| C(16)-C(17) | 1.422(3) |
| C(16)-Ru(2) | 2.212(2) |
| C(16)-H(16) | 0.9800 |
| C(17)-Ru(2) | 2.210(2) |
| C(17)-H(17) | 0.9800 |
| C(18)-O(3) | 1.138(3) |
| C(18)-Ru(2) | 1.896(2) |
| C(19)-O(4) | 1.137(3) |
| C(19)-Ru(2) | 1.902(2) |
| C(20)-N(2) | 1.489(3) |
| C(20)-C(21) | 1.520(3) |
| C(20)-H(20A) | 0.9700 |
| C(20)-H(20B) | 0.9700 |
| C(21)-C(22) | 1.530(3) |
| C(21)-H(21A) | 0.9700 |
| C(21)-H(21B) | 0.9700 |

| | |
|---|---|
| C(22)-C(23) | 1.523(3) |
| C(22)-H(22A) | 0.9700 |
| C(22)-H(22B) | 0.9700 |
| C(23)-C(24) | 1.521(3) |
| C(23)-H(23A) | 0.9700 |
| C(23)-H(23B) | 0.9700 |
| C(24)-H(24A) | 0.9600 |
| C(24)-H(24B) | 0.9600 |
| C(24)-H(24C) | 0.9600 |
| B(1)-F(2) | 1.381(3) |
| B(1)-F(3) | 1.384(3) |
| B(1)-F(1) | 1.398(3) |
| B(1)-F(4) | 1.401(3) |
| B(2)-F(8) | 1.371(3) |
| B(2)-F(5) | 1.391(3) |
| B(2)-F(7) | 1.395(3) |
| B(2)-F(6) | 1.399(3) |
| N(1)-Ru(1) | 2.1484(18) |
| N(1)-H(1A) | 0.9000 |
| N(1)-H(1B) | 0.9000 |
| N(2)-Ru(2) | 2.1452(18) |
| N(2)-H(2A) | 0.9000 |
| N(2)-H(2B) | 0.9000 |

| | |
|---|---|
| C(5)-C(1)-C(2) | 107.7(2) |
| C(5)-C(1)-Ru(1) | 71.26(14) |
| C(2)-C(1)-Ru(1) | 72.65(13) |
| C(5)-C(1)-H(1) | 126.0 |
| C(2)-C(1)-H(1) | 126.0 |
| Ru(1)-C(1)-H(1) | 126.1 |
| C(3)-C(2)-C(1) | 107.8(2) |
| C(3)-C(2)-Ru(1) | 72.52(13) |
| C(1)-C(2)-Ru(1) | 69.70(13) |
| C(3)-C(2)-H(2) | 126.0 |
| C(1)-C(2)-H(2) | 126.1 |
| Ru(1)-C(2)-H(2) | 126.0 |
| C(2)-C(3)-C(4) | 108.7(2) |
| C(2)-C(3)-Ru(1) | 70.93(13) |

| | |
|---|---|
| C(4)-C(3)-Ru(1) | 70.67(13) |
| C(2)-C(3)-H(3) | 125.6 |
| C(4)-C(3)-H(3) | 125.7 |
| Ru(1)-C(3)-H(3) | 125.6 |
| C(3)-C(4)-C(5) | 107.7(2) |
| C(3)-C(4)-Ru(1) | 72.47(13) |
| C(5)-C(4)-Ru(1) | 70.06(13) |
| C(3)-C(4)-H(4) | 126.1 |
| C(5)-C(4)-H(4) | 126.1 |
| Ru(1)-C(4)-H(4) | 126.1 |
| C(4)-C(5)-C(1) | 108.2(2) |
| C(4)-C(5)-Ru(1) | 72.57(14) |
| C(1)-C(5)-Ru(1) | 71.03(13) |
| C(4)-C(5)-H(5) | 125.8 |
| C(1)-C(5)-H(5) | 125.9 |
| Ru(1)-C(5)-H(5) | 125.8 |
| O(1)-C(6)-Ru(1) | 175.7(2) |
| O(2)-C(7)-Ru(1) | 174.7(2) |
| N(1)-C(8)-C(9) | 113.16(18) |
| N(1)-C(8)-H(8A) | 108.9 |
| C(9)-C(8)-H(8A) | 108.9 |
| N(1)-C(8)-H(8B) | 108.9 |
| C(9)-C(8)-H(8B) | 108.9 |
| H(8A)-C(8)-H(8B) | 107.8 |
| C(8)-C(9)-C(10) | 110.75(18) |
| C(8)-C(9)-H(9A) | 109.5 |
| C(10)-C(9)-H(9A) | 109.5 |
| C(8)-C(9)-H(9B) | 109.5 |
| C(10)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 108.1 |
| C(9)-C(10)-C(11) | 114.81(19) |
| C(9)-C(10)-H(10A) | 108.6 |
| C(11)-C(10)-H(10A) | 108.6 |
| C(9)-C(10)-H(10B) | 108.6 |
| C(11)-C(10)-H(10B) | 108.6 |
| H(10A)-C(10)-H(10B) | 107.5 |
| C(12)-C(11)-C(10) | 113.85(19) |
| C(12)-C(11)-H(11A) | 108.8 |

| | |
|---|---|
| C(10)-C(11)-H(11A) | 108.8 |
| C(12)-C(11)-H(11B) | 108.8 |
| C(10)-C(11)-H(11B) | 108.8 |
| H(11A)-C(11)-H(11B) | 107.7 |
| C(11)-C(12)-H(12A) | 109.5 |
| C(11)-C(12)-H(12B) | 109.5 |
| H(12A)-C(12)-H(12B) | 109.5 |
| C(11)-C(12)-H(12C) | 109.5 |
| H(12A)-C(12)-H(12C) | 109.5 |
| H(12B)-C(12)-H(12C) | 109.5 |
| C(14)-C(13)-C(17) | 107.8(2) |
| C(14)-C(13)-Ru(2) | 71.98(13) |
| C(17)-C(13)-Ru(2) | 69.66(12) |
| C(14)-C(13)-H(13) | 126.0 |
| C(17)-C(13)-H(13) | 126.1 |
| Ru(2)-C(13)-H(13) | 126.0 |
| C(13)-C(14)-C(15) | 108.7(2) |
| C(13)-C(14)-Ru(2) | 71.52(13) |
| C(15)-C(14)-Ru(2) | 70.39(13) |
| C(13)-C(14)-H(14) | 125.6 |
| C(15)-C(14)-H(14) | 125.6 |
| Ru(2)-C(14)-H(14) | 125.6 |
| C(16)-C(15)-C(14) | 107.4(2) |
| C(16)-C(15)-Ru(2) | 70.65(13) |
| C(14)-C(15)-Ru(2) | 72.48(13) |
| C(16)-C(15)-H(15) | 126.2 |
| C(14)-C(15)-H(15) | 126.2 |
| Ru(2)-C(15)-H(15) | 126.2 |
| C(17)-C(16)-C(15) | 108.5(2) |
| C(17)-C(16)-Ru(2) | 71.16(13) |
| C(15)-C(16)-Ru(2) | 71.96(13) |
| C(17)-C(16)-H(16) | 125.7 |
| C(15)-C(16)-H(16) | 125.7 |
| Ru(2)-C(16)-H(16) | 125.7 |
| C(16)-C(17)-C(13) | 107.5(2) |
| C(16)-C(17)-Ru(2) | 71.31(13) |
| C(13)-C(17)-Ru(2) | 72.73(13) |
| C(16)-C(17)-H(17) | 126.1 |

| | |
|---|---|
| C(13)-C(17)-H(17) | 126.1 |
| Ru(2)-C(17)-H(17) | 126.1 |
| O(3)-C(18)-Ru(2) | 176.5(2) |
| O(4)-C(19)-Ru(2) | 176.0(2) |
| N(2)-C(20)-C(21) | 111.85(18) |
| N(2)-C(20)-H(20A) | 109.2 |
| C(21)-C(20)-H(20A) | 109.2 |
| N(2)-C(20)-H(20B) | 109.2 |
| C(21)-C(20)-H(20B) | 109.2 |
| H(20A)-C(20)-H(20B) | 107.9 |
| C(20)-C(21)-C(22) | 112.08(18) |
| C(20)-C(21)-H(21A) | 109.2 |
| C(22)-C(21)-H(21A) | 109.2 |
| C(20)-C(21)-H(21B) | 109.2 |
| C(22)-C(21)-H(21B) | 109.2 |
| H(21A)-C(21)-H(21B) | 107.9 |
| C(23)-C(22)-C(21) | 113.05(19) |
| C(23)-C(22)-H(22A) | 109.0 |
| C(21)-C(22)-H(22A) | 109.0 |
| C(23)-C(22)-H(22B) | 109.0 |
| C(21)-C(22)-H(22B) | 109.0 |
| H(22A)-C(22)-H(22B) | 107.8 |
| C(24)-C(23)-C(22) | 113.2(2) |
| C(24)-C(23)-H(23A) | 108.9 |
| C(22)-C(23)-H(23A) | 108.9 |
| C(24)-C(23)-H(23B) | 108.9 |
| C(22)-C(23)-H(23B) | 108.9 |
| H(23A)-C(23)-H(23B) | 107.7 |
| C(23)-C(24)-H(24A) | 109.5 |
| C(23)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| C(23)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |
| F(2)-B(1)-F(3) | 110.7(2) |
| F(2)-B(1)-F(1) | 109.7(2) |
| F(3)-B(1)-F(1) | 110.5(2) |
| F(2)-B(1)-F(4) | 108.5(2) |

| | |
|---|---|
| F(3)-B(1)-F(4) | 108.4(2) |
| F(1)-B(1)-F(4) | 109.0(2) |
| F(8)-B(2)-F(5) | 110.3(2) |
| F(8)-B(2)-F(7) | 110.2(2) |
| F(5)-B(2)-F(7) | 111.0(2) |
| F(8)-B(2)-F(6) | 108.9(2) |
| F(5)-B(2)-F(6) | 108.7(2) |
| F(7)-B(2)-F(6) | 107.65(19) |
| C(8)-N(1)-Ru(1) | 116.38(14) |
| C(8)-N(1)-H(1A) | 108.2 |
| Ru(1)-N(1)-H(1A) | 108.2 |
| C(8)-N(1)-H(1B) | 108.2 |
| Ru(1)-N(1)-H(1B) | 108.2 |
| H(1A)-N(1)-H(1B) | 107.4 |
| C(20)-N(2)-Ru(2) | 117.54(14) |
| C(20)-N(2)-H(2A) | 107.9 |
| Ru(2)-N(2)-H(2A) | 107.9 |
| C(20)-N(2)-H(2B) | 107.9 |
| Ru(2)-N(2)-H(2B) | 107.9 |
| H(2A)-N(2)-H(2B) | 107.2 |
| C(6)-Ru(1)-C(7) | 91.51(10) |
| C(6)-Ru(1)-N(1) | 91.44(8) |
| C(7)-Ru(1)-N(1) | 92.33(8) |
| C(6)-Ru(1)-C(1) | 117.75(10) |
| C(7)-Ru(1)-C(1) | 93.50(9) |
| N(1)-Ru(1)-C(1) | 150.02(8) |
| C(6)-Ru(1)-C(5) | 92.56(10) |
| C(7)-Ru(1)-C(5) | 124.02(10) |
| N(1)-Ru(1)-C(5) | 143.27(9) |
| C(1)-Ru(1)-C(5) | 37.71(9) |
| C(6)-Ru(1)-C(4) | 103.06(10) |
| C(7)-Ru(1)-C(4) | 155.72(9) |
| N(1)-Ru(1)-C(4) | 106.41(9) |
| C(1)-Ru(1)-C(4) | 62.59(9) |
| C(5)-Ru(1)-C(4) | 37.37(10) |
| C(6)-Ru(1)-C(2) | 154.18(9) |
| C(7)-Ru(1)-C(2) | 96.99(9) |
| N(1)-Ru(1)-C(2) | 112.42(8) |

| | |
|---|---|
| C(1)-Ru(1)-C(2) | 37.64(9) |
| C(5)-Ru(1)-C(2) | 62.54(9) |
| C(4)-Ru(1)-C(2) | 61.91(9) |
| C(6)-Ru(1)-C(3) | 138.45(9) |
| C(7)-Ru(1)-C(3) | 129.66(10) |
| N(1)-Ru(1)-C(3) | 92.10(8) |
| C(1)-Ru(1)-C(3) | 61.99(9) |
| C(5)-Ru(1)-C(3) | 61.91(9) |
| C(4)-Ru(1)-C(3) | 36.86(9) |
| C(2)-Ru(1)-C(3) | 36.56(8) |
| C(18)-Ru(2)-C(19) | 91.33(10) |
| C(18)-Ru(2)-N(2) | 90.49(8) |
| C(19)-Ru(2)-N(2) | 91.74(8) |
| C(18)-Ru(2)-C(17) | 113.42(9) |
| C(19)-Ru(2)-C(17) | 97.41(9) |
| N(2)-Ru(2)-C(17) | 154.03(8) |
| C(18)-Ru(2)-C(16) | 91.98(9) |
| C(19)-Ru(2)-C(16) | 130.38(9) |
| N(2)-Ru(2)-C(16) | 137.69(8) |
| C(17)-Ru(2)-C(16) | 37.53(8) |
| C(18)-Ru(2)-C(15) | 106.44(9) |
| C(19)-Ru(2)-C(15) | 157.21(9) |
| N(2)-Ru(2)-C(15) | 102.04(8) |
| C(17)-Ru(2)-C(15) | 62.73(9) |
| C(16)-Ru(2)-C(15) | 37.39(9) |
| C(18)-Ru(2)-C(13) | 150.84(9) |
| C(19)-Ru(2)-C(13) | 95.56(9) |
| N(2)-Ru(2)-C(13) | 117.49(8) |
| C(17)-Ru(2)-C(13) | 37.60(8) |
| C(16)-Ru(2)-C(13) | 62.24(9) |
| C(15)-Ru(2)-C(13) | 62.01(9) |
| C(18)-Ru(2)-C(14) | 143.13(9) |
| C(19)-Ru(2)-C(14) | 125.21(10) |
| N(2)-Ru(2)-C(14) | 92.87(8) |
| C(17)-Ru(2)-C(14) | 62.07(8) |
| C(16)-Ru(2)-C(14) | 61.89(9) |
| C(15)-Ru(2)-C(14) | 37.13(9) |
| C(13)-Ru(2)-C(14) | 36.50(8) |

**Table 33:** Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_4CH_3]BF_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 18(1) | 36(1) | 17(1) | 6(1) | 5(1) | 7(1) |
| C(2) | 14(1) | 25(1) | 21(1) | -3(1) | 2(1) | 1(1) |
| C(3) | 13(1) | 41(1) | 21(1) | 5(1) | 6(1) | 2(1) |
| C(4) | 17(1) | 38(1) | 26(1) | -12(1) | 5(1) | 7(1) |
| C(5) | 20(1) | 22(1) | 38(1) | 5(1) | 7(1) | 5(1) |
| C(6) | 20(1) | 24(1) | 18(1) | 0(1) | 8(1) | 1(1) |
| C(7) | 16(1) | 25(1) | 17(1) | 1(1) | 6(1) | 2(1) |
| C(8) | 23(1) | 20(1) | 18(1) | 0(1) | 5(1) | -3(1) |
| C(9) | 18(1) | 21(1) | 18(1) | 1(1) | 6(1) | -1(1) |
| C(10) | 22(1) | 23(1) | 20(1) | -3(1) | 9(1) | -3(1) |
| C(11) | 23(1) | 18(1) | 24(1) | -2(1) | 9(1) | 1(1) |
| C(12) | 43(2) | 32(1) | 26(1) | 4(1) | 17(1) | 9(1) |
| C(13) | 15(1) | 24(1) | 19(1) | -2(1) | 2(1) | 0(1) |
| C(14) | 13(1) | 34(1) | 21(1) | 3(1) | 6(1) | 2(1) |
| C(15) | 16(1) | 32(1) | 23(1) | -4(1) | 6(1) | 7(1) |
| C(16) | 20(1) | 22(1) | 26(1) | 1(1) | 5(1) | 5(1) |
| C(17) | 19(1) | 25(1) | 16(1) | 3(1) | 4(1) | 3(1) |
| C(18) | 20(1) | 23(1) | 19(1) | 1(1) | 10(1) | 3(1) |
| C(19) | 22(1) | 26(1) | 15(1) | 2(1) | 7(1) | 2(1) |
| C(20) | 17(1) | 19(1) | 19(1) | -1(1) | 5(1) | -2(1) |
| C(21) | 16(1) | 21(1) | 19(1) | 0(1) | 5(1) | -2(1) |
| C(22) | 19(1) | 19(1) | 22(1) | -2(1) | 9(1) | -2(1) |
| C(23) | 21(1) | 21(1) | 22(1) | -1(1) | 6(1) | -3(1) |
| C(24) | 30(1) | 21(1) | 30(1) | 2(1) | 12(1) | -1(1) |
| B(1) | 22(1) | 23(1) | 22(1) | 0(1) | 12(1) | 1(1) |
| B(2) | 20(1) | 23(1) | 21(1) | 1(1) | 12(1) | -1(1) |
| F(1) | 28(1) | 32(1) | 32(1) | 7(1) | 19(1) | 9(1) |
| F(2) | 35(1) | 28(1) | 51(1) | -12(1) | 13(1) | -8(1) |
| F(3) | 72(1) | 45(1) | 55(1) | 17(1) | 53(1) | 20(1) |
| F(4) | 18(1) | 49(1) | 32(1) | -14(1) | 7(1) | 0(1) |
| F(5) | 33(1) | 34(1) | 41(1) | 12(1) | 26(1) | 12(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| F(6) | 21(1) | 59(1) | 24(1) | 6(1) | 10(1) | 8(1) |
| F(7) | 40(1) | 36(1) | 41(1) | 13(1) | 31(1) | 5(1) |
| F(8) | 48(1) | 48(1) | 54(1) | -29(1) | 34(1) | -26(1) |
| N(1) | 14(1) | 21(1) | 16(1) | 1(1) | 6(1) | -1(1) |
| N(2) | 14(1) | 19(1) | 16(1) | -1(1) | 6(1) | -1(1) |
| O(1) | 26(1) | 32(1) | 30(1) | -5(1) | 12(1) | -10(1) |
| O(2) | 29(1) | 36(1) | 26(1) | -2(1) | 15(1) | 8(1) |
| O(3) | 23(1) | 29(1) | 34(1) | -3(1) | 13(1) | -8(1) |
| O(4) | 37(1) | 32(1) | 28(1) | -1(1) | 19(1) | 10(1) |
| Ru(1) | 13(1) | 18(1) | 13(1) | -1(1) | 5(1) | 0(1) |
| Ru(2) | 13(1) | 18(1) | 13(1) | -1(1) | 6(1) | 0(1) |

**Table 34:** Torsion angles [°] for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2(CH_2)_4CH_3]BF_4$.

| | |
|---|---|
| C(5)-C(1)-C(2)-C(3) | 0.1(3) |
| Ru(1)-C(1)-C(2)-C(3) | -62.94(16) |
| C(5)-C(1)-C(2)-Ru(1) | 63.06(16) |
| C(1)-C(2)-C(3)-C(4) | 0.3(3) |
| Ru(1)-C(2)-C(3)-C(4) | -60.86(16) |
| C(1)-C(2)-C(3)-Ru(1) | 61.13(15) |
| C(2)-C(3)-C(4)-C(5) | -0.6(3) |
| Ru(1)-C(3)-C(4)-C(5) | -61.58(16) |
| C(2)-C(3)-C(4)-Ru(1) | 61.02(16) |
| C(3)-C(4)-C(5)-C(1) | 0.6(3) |
| Ru(1)-C(4)-C(5)-C(1) | -62.52(16) |
| C(3)-C(4)-C(5)-Ru(1) | 63.15(17) |
| C(2)-C(1)-C(5)-C(4) | -0.5(3) |
| Ru(1)-C(1)-C(5)-C(4) | 63.51(17) |
| C(2)-C(1)-C(5)-Ru(1) | -63.98(16) |
| N(1)-C(8)-C(9)-C(10) | -178.62(18) |
| C(8)-C(9)-C(10)-C(11) | -176.68(19) |
| C(9)-C(10)-C(11)-C(12) | -64.2(3) |
| C(17)-C(13)-C(14)-C(15) | -0.1(3) |
| Ru(2)-C(13)-C(14)-C(15) | -60.87(16) |
| C(17)-C(13)-C(14)-Ru(2) | 60.75(15) |
| C(13)-C(14)-C(15)-C(16) | -0.8(3) |
| Ru(2)-C(14)-C(15)-C(16) | -62.42(16) |
| C(13)-C(14)-C(15)-Ru(2) | 61.58(16) |
| C(14)-C(15)-C(16)-C(17) | 1.5(3) |
| Ru(2)-C(15)-C(16)-C(17) | -62.13(16) |
| C(14)-C(15)-C(16)-Ru(2) | 63.62(16) |
| C(15)-C(16)-C(17)-C(13) | -1.6(3) |
| Ru(2)-C(16)-C(17)-C(13) | -64.21(15) |
| C(15)-C(16)-C(17)-Ru(2) | 62.64(16) |
| C(14)-C(13)-C(17)-C(16) | 1.0(3) |
| Ru(2)-C(13)-C(17)-C(16) | 63.28(16) |
| C(14)-C(13)-C(17)-Ru(2) | -62.23(16) |
| N(2)-C(20)-C(21)-C(22) | -170.46(17) |
| C(20)-C(21)-C(22)-C(23) | 177.84(19) |
| C(21)-C(22)-C(23)-C(24) | -173.66(19) |

| | |
|---|---|
| C(9)-C(8)-N(1)-Ru(1) | -173.91(14) |
| C(21)-C(20)-N(2)-Ru(2) | -172.20(14) |
| O(1)-C(6)-Ru(1)-C(7) | -98(3) |
| O(1)-C(6)-Ru(1)-N(1) | 170(3) |
| O(1)-C(6)-Ru(1)-C(1) | -3(3) |
| O(1)-C(6)-Ru(1)-C(5) | 26(3) |
| O(1)-C(6)-Ru(1)-C(4) | 63(3) |
| O(1)-C(6)-Ru(1)-C(2) | 12(3) |
| O(1)-C(6)-Ru(1)-C(3) | 75(3) |
| O(2)-C(7)-Ru(1)-C(6) | 109(2) |
| O(2)-C(7)-Ru(1)-N(1) | -160(2) |
| O(2)-C(7)-Ru(1)-C(1) | -9(2) |
| O(2)-C(7)-Ru(1)-C(5) | 14(2) |
| O(2)-C(7)-Ru(1)-C(4) | -19(2) |
| O(2)-C(7)-Ru(1)-C(2) | -47(2) |
| O(2)-C(7)-Ru(1)-C(3) | -65(2) |
| C(8)-N(1)-Ru(1)-C(6) | 145.25(16) |
| C(8)-N(1)-Ru(1)-C(7) | 53.69(16) |
| C(8)-N(1)-Ru(1)-C(1) | -47.4(2) |
| C(8)-N(1)-Ru(1)-C(5) | -118.52(18) |
| C(8)-N(1)-Ru(1)-C(4) | -110.68(16) |
| C(8)-N(1)-Ru(1)-C(2) | -44.85(17) |
| C(8)-N(1)-Ru(1)-C(3) | -76.15(16) |
| C(5)-C(1)-Ru(1)-C(6) | 53.30(17) |
| C(2)-C(1)-Ru(1)-C(6) | 169.55(13) |
| C(5)-C(1)-Ru(1)-C(7) | 146.85(15) |
| C(2)-C(1)-Ru(1)-C(7) | -96.90(15) |
| C(5)-C(1)-Ru(1)-N(1) | -112.35(19) |
| C(2)-C(1)-Ru(1)-N(1) | 3.9(2) |
| C(2)-C(1)-Ru(1)-C(5) | 116.2(2) |
| C(5)-C(1)-Ru(1)-C(4) | -37.55(15) |
| C(2)-C(1)-Ru(1)-C(4) | 78.70(15) |
| C(5)-C(1)-Ru(1)-C(2) | -116.2(2) |
| C(5)-C(1)-Ru(1)-C(3) | -79.39(16) |
| C(2)-C(1)-Ru(1)-C(3) | 36.86(13) |
| C(4)-C(5)-Ru(1)-C(6) | 108.30(16) |
| C(1)-C(5)-Ru(1)-C(6) | -134.75(15) |
| C(4)-C(5)-Ru(1)-C(7) | -158.15(15) |

| | |
|---|---|
| C(1)-C(5)-Ru(1)-C(7) | -41.19(18) |
| C(4)-C(5)-Ru(1)-N(1) | 12.4(2) |
| C(1)-C(5)-Ru(1)-N(1) | 129.40(16) |
| C(4)-C(5)-Ru(1)-C(1) | -117.0(2) |
| C(1)-C(5)-Ru(1)-C(4) | 117.0(2) |
| C(4)-C(5)-Ru(1)-C(2) | -78.84(15) |
| C(1)-C(5)-Ru(1)-C(2) | 38.12(14) |
| C(4)-C(5)-Ru(1)-C(3) | -37.32(14) |
| C(1)-C(5)-Ru(1)-C(3) | 79.64(15) |
| C(3)-C(4)-Ru(1)-C(6) | 166.24(15) |
| C(5)-C(4)-Ru(1)-C(6) | -76.82(16) |
| C(3)-C(4)-Ru(1)-C(7) | -68.3(3) |
| C(5)-C(4)-Ru(1)-C(7) | 48.6(3) |
| C(3)-C(4)-Ru(1)-N(1) | 70.78(15) |
| C(5)-C(4)-Ru(1)-N(1) | -172.28(14) |
| C(3)-C(4)-Ru(1)-C(1) | -79.04(15) |
| C(5)-C(4)-Ru(1)-C(1) | 37.90(15) |
| C(3)-C(4)-Ru(1)-C(5) | -116.9(2) |
| C(3)-C(4)-Ru(1)-C(2) | -36.29(14) |
| C(5)-C(4)-Ru(1)-C(2) | 80.65(16) |
| C(5)-C(4)-Ru(1)-C(3) | 116.9(2) |
| C(3)-C(2)-Ru(1)-C(6) | 95.6(2) |
| C(1)-C(2)-Ru(1)-C(6) | -21.6(3) |
| C(3)-C(2)-Ru(1)-C(7) | -156.10(15) |
| C(1)-C(2)-Ru(1)-C(7) | 86.67(15) |
| C(3)-C(2)-Ru(1)-N(1) | -60.66(16) |
| C(1)-C(2)-Ru(1)-N(1) | -177.89(13) |
| C(3)-C(2)-Ru(1)-C(1) | 117.2(2) |
| C(3)-C(2)-Ru(1)-C(5) | 79.04(16) |
| C(1)-C(2)-Ru(1)-C(5) | -38.19(14) |
| C(3)-C(2)-Ru(1)-C(4) | 36.59(15) |
| C(1)-C(2)-Ru(1)-C(4) | -80.64(15) |
| C(1)-C(2)-Ru(1)-C(3) | -117.2(2) |
| C(2)-C(3)-Ru(1)-C(6) | -139.20(16) |
| C(4)-C(3)-Ru(1)-C(6) | -20.4(2) |
| C(2)-C(3)-Ru(1)-C(7) | 31.49(19) |
| C(4)-C(3)-Ru(1)-C(7) | 150.25(15) |
| C(2)-C(3)-Ru(1)-N(1) | 126.26(14) |

| | |
|---|---|
| C(4)-C(3)-Ru(1)-N(1) | -114.98(15) |
| C(2)-C(3)-Ru(1)-C(1) | -37.96(14) |
| C(4)-C(3)-Ru(1)-C(1) | 80.80(16) |
| C(2)-C(3)-Ru(1)-C(5) | -80.92(16) |
| C(4)-C(3)-Ru(1)-C(5) | 37.83(15) |
| C(2)-C(3)-Ru(1)-C(4) | -118.8(2) |
| C(4)-C(3)-Ru(1)-C(2) | 118.8(2) |
| O(3)-C(18)-Ru(2)-C(19) | -100(3) |
| O(3)-C(18)-Ru(2)-N(2) | 168(3) |
| O(3)-C(18)-Ru(2)-C(17) | -1(3) |
| O(3)-C(18)-Ru(2)-C(16) | 30(3) |
| O(3)-C(18)-Ru(2)-C(15) | 66(3) |
| O(3)-C(18)-Ru(2)-C(13) | 4(3) |
| O(3)-C(18)-Ru(2)-C(14) | 73(3) |
| O(4)-C(19)-Ru(2)-C(18) | 107(3) |
| O(4)-C(19)-Ru(2)-N(2) | -162(3) |
| O(4)-C(19)-Ru(2)-C(17) | -7(3) |
| O(4)-C(19)-Ru(2)-C(16) | 13(3) |
| O(4)-C(19)-Ru(2)-C(15) | -35(3) |
| O(4)-C(19)-Ru(2)-C(13) | -44(3) |
| O(4)-C(19)-Ru(2)-C(14) | -67(3) |
| C(20)-N(2)-Ru(2)-C(18) | 153.37(15) |
| C(20)-N(2)-Ru(2)-C(19) | 62.03(16) |
| C(20)-N(2)-Ru(2)-C(17) | -48.9(2) |
| C(20)-N(2)-Ru(2)-C(16) | -113.14(17) |
| C(20)-N(2)-Ru(2)-C(15) | -99.70(15) |
| C(20)-N(2)-Ru(2)-C(13) | -35.16(17) |
| C(20)-N(2)-Ru(2)-C(14) | -63.36(15) |
| C(16)-C(17)-Ru(2)-C(18) | 59.88(16) |
| C(13)-C(17)-Ru(2)-C(18) | 175.81(13) |
| C(16)-C(17)-Ru(2)-C(19) | 154.57(15) |
| C(13)-C(17)-Ru(2)-C(19) | -89.50(14) |
| C(16)-C(17)-Ru(2)-N(2) | -95.7(2) |
| C(13)-C(17)-Ru(2)-N(2) | 20.2(2) |
| C(13)-C(17)-Ru(2)-C(16) | 115.9(2) |
| C(16)-C(17)-Ru(2)-C(15) | -37.23(14) |
| C(13)-C(17)-Ru(2)-C(15) | 78.70(14) |
| C(16)-C(17)-Ru(2)-C(13) | -115.9(2) |

| | |
|---|---|
| C(16)-C(17)-Ru(2)-C(14) | -79.33(15) |
| C(13)-C(17)-Ru(2)-C(14) | 36.60(13) |
| C(17)-C(16)-Ru(2)-C(18) | -127.42(14) |
| C(15)-C(16)-Ru(2)-C(18) | 114.90(15) |
| C(17)-C(16)-Ru(2)-C(19) | -33.98(19) |
| C(15)-C(16)-Ru(2)-C(19) | -151.67(15) |
| C(17)-C(16)-Ru(2)-N(2) | 139.67(13) |
| C(15)-C(16)-Ru(2)-N(2) | 22.0(2) |
| C(15)-C(16)-Ru(2)-C(17) | -117.7(2) |
| C(17)-C(16)-Ru(2)-C(15) | 117.7(2) |
| C(17)-C(16)-Ru(2)-C(13) | 38.32(13) |
| C(15)-C(16)-Ru(2)-C(13) | -79.36(15) |
| C(17)-C(16)-Ru(2)-C(14) | 79.84(15) |
| C(15)-C(16)-Ru(2)-C(14) | -37.84(14) |
| C(16)-C(15)-Ru(2)-C(18) | -70.93(16) |
| C(14)-C(15)-Ru(2)-C(18) | 172.78(14) |
| C(16)-C(15)-Ru(2)-C(19) | 68.9(3) |
| C(14)-C(15)-Ru(2)-C(19) | -47.4(3) |
| C(16)-C(15)-Ru(2)-N(2) | -165.07(14) |
| C(14)-C(15)-Ru(2)-N(2) | 78.64(14) |
| C(16)-C(15)-Ru(2)-C(17) | 37.37(14) |
| C(14)-C(15)-Ru(2)-C(17) | -78.92(15) |
| C(14)-C(15)-Ru(2)-C(16) | -116.3(2) |
| C(16)-C(15)-Ru(2)-C(13) | 80.03(15) |
| C(14)-C(15)-Ru(2)-C(13) | -36.26(13) |
| C(16)-C(15)-Ru(2)-C(14) | 116.3(2) |
| C(14)-C(13)-Ru(2)-C(18) | 109.8(2) |
| C(17)-C(13)-Ru(2)-C(18) | -7.9(2) |
| C(14)-C(13)-Ru(2)-C(19) | -147.40(15) |
| C(17)-C(13)-Ru(2)-C(19) | 94.93(14) |
| C(14)-C(13)-Ru(2)-N(2) | -52.52(16) |
| C(17)-C(13)-Ru(2)-N(2) | -170.18(12) |
| C(14)-C(13)-Ru(2)-C(17) | 117.7(2) |
| C(14)-C(13)-Ru(2)-C(16) | 79.41(15) |
| C(17)-C(13)-Ru(2)-C(16) | -38.25(13) |
| C(14)-C(13)-Ru(2)-C(15) | 36.89(14) |
| C(17)-C(13)-Ru(2)-C(15) | -80.77(15) |
| C(17)-C(13)-Ru(2)-C(14) | -117.7(2) |

| | |
|---|---|
| C(13)-C(14)-Ru(2)-C(18) | -130.16(17) |
| C(15)-C(14)-Ru(2)-C(18) | -11.6(2) |
| C(13)-C(14)-Ru(2)-C(19) | 41.01(18) |
| C(15)-C(14)-Ru(2)-C(19) | 159.59(14) |
| C(13)-C(14)-Ru(2)-N(2) | 135.18(14) |
| C(15)-C(14)-Ru(2)-N(2) | -106.25(14) |
| C(13)-C(14)-Ru(2)-C(17) | -37.71(14) |
| C(15)-C(14)-Ru(2)-C(17) | 80.86(15) |
| C(13)-C(14)-Ru(2)-C(16) | -80.46(15) |
| C(15)-C(14)-Ru(2)-C(16) | 38.12(14) |
| C(13)-C(14)-Ru(2)-C(15) | -118.6(2) |
| C(15)-C(14)-Ru(2)-C(13) | 118.6(2) |

# STRUCTURE TABLES PERTAINING TO CHAPTER 4

## Pentamethycyclopentadienyl ruthenium(II) ethylamine complex - $[\eta^5\text{-}C_5(CH_3)_5Ru(CO)_2NH_2CH_2CH_3]BF_4$

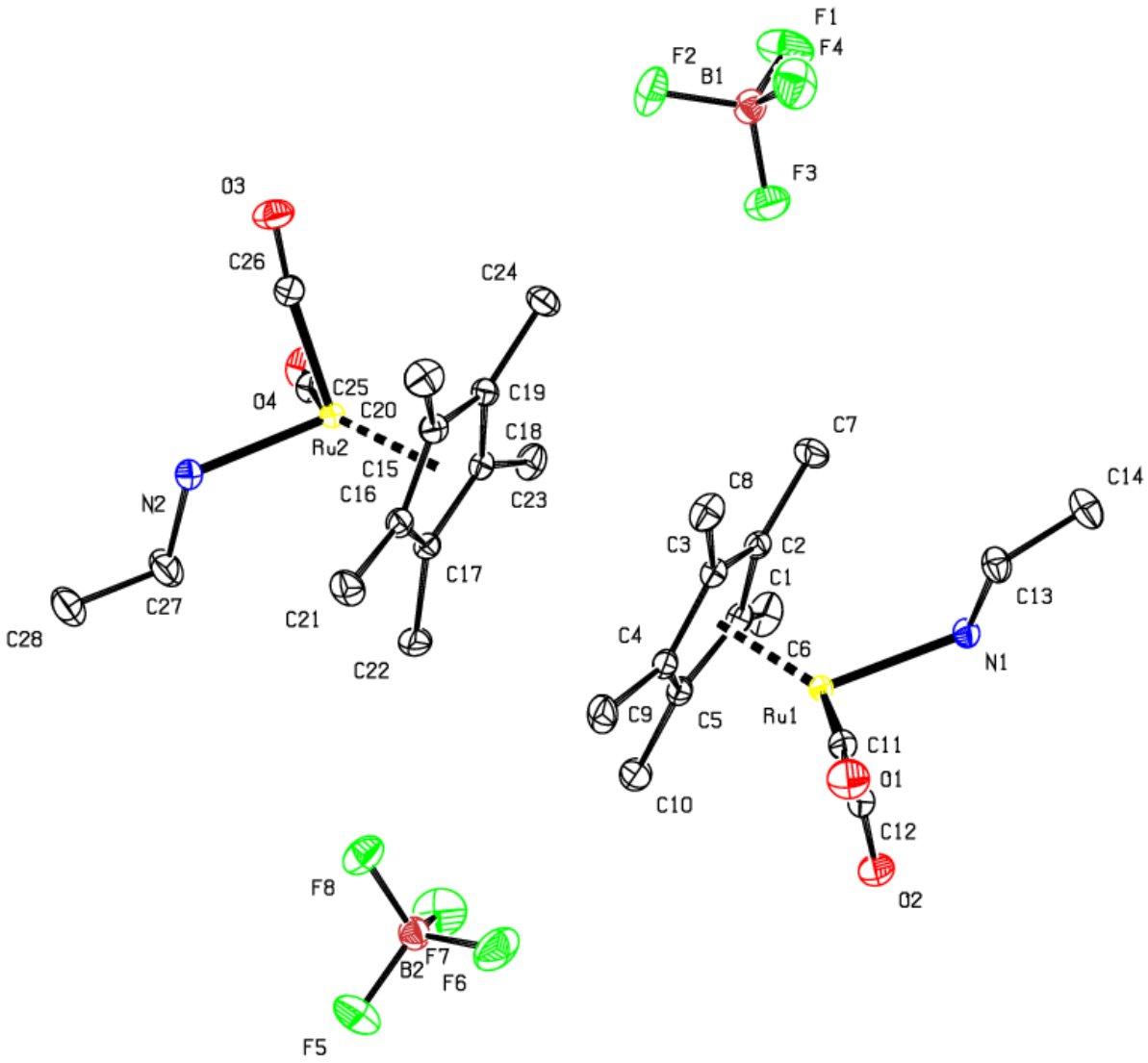


**Table B35.** Crystal data and structure refinement for $[\eta^5\text{-}C_5(CH_3)_5Ru(CO)_2NH_2CH_2CH_3]BF_4$.

| | | |
|---|---|---|
| Empirical formula | C14 H22 B F4 N O2 Ru | |
| Formula weight | 424.21 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 10.5561(2) Å | α= 106.1380(10)°. |
| | b = 11.3098(3) Å | β= 99.5730(10)°. |
| | c = 16.0927(4) Å | γ = 105.3010(10)°. |
| Volume | 1719.56(7) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.639 $Mg/m^3$ | |
| Absorption coefficient | 0.957 $mm^{-1}$ | |
| F(000) | 856 | |
| Crystal size | 0.46 x 0.24 x 0.12 $mm^3$ | |
| Theta range for data collection | 1.36 to 28.42°. | |
| Index ranges | -14<=h<=14, -14<=k<=15, -21<=l<=21 | |
| Reflections collected | 44322 | |
| Independent reflections | 8618 [R(int) = 0.0206] | |
| Completeness to theta = 28.42° | 99.4 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.8939 and 0.6674 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 8618 / 7 / 427 | |
| Goodness-of-fit on $F^2$ | 1.025 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0165, wR2 = 0.0415 | |
| R indices (all data) | R1 = 0.0193, wR2 = 0.0437 | |
| Largest diff. peak and hole | 0.469 and -0.487 $e.Å^{-3}$ | |

**Table B36:** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $[\eta^5\text{-}C_5(CH_3)_5Ru(CO)_2NH_2CH_2CH_3]BF_4$. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 2626(1) | 2248(1) | 1218(1) | 16(1) |
| C(2) | 2850(1) | 3138(1) | 2097(1) | 15(1) |
| C(3) | 4216(1) | 4003(1) | 2381(1) | 15(1) |
| C(4) | 4869(1) | 3627(1) | 1673(1) | 16(1) |
| C(5) | 3894(1) | 2534(1) | 964(1) | 17(1) |
| C(6) | 1371(1) | 1106(1) | 698(1) | 26(1) |
| C(7) | 1818(1) | 3117(1) | 2633(1) | 24(1) |
| C(8) | 4912(1) | 4997(1) | 3293(1) | 23(1) |
| C(9) | 6348(1) | 4217(1) | 1738(1) | 26(1) |
| C(10) | 4122(2) | 1720(1) | 129(1) | 26(1) |
| C(11) | 4326(1) | 5927(1) | 1251(1) | 19(1) |
| C(12) | 2557(1) | 3769(1) | -140(1) | 19(1) |
| C(13) | 1695(1) | 5992(1) | 2159(1) | 20(1) |
| C(14) | 352(1) | 6106(1) | 2320(1) | 27(1) |
| O(1) | 5089(1) | 6904(1) | 1338(1) | 30(1) |
| O(2) | 2240(1) | 3394(1) | -901(1) | 27(1) |
| Ru(1) | 3181(1) | 4240(1) | 1125(1) | 12(1) |
| N(1) | 1507(1) | 4946(1) | 1302(1) | 16(1) |
| C(15) | -3040(1) | 2892(1) | 4184(1) | 16(1) |
| C(16) | -2580(1) | 2527(1) | 3399(1) | 16(1) |
| C(17) | -3691(1) | 1512(1) | 2702(1) | 16(1) |
| C(18) | -4855(1) | 1289(1) | 3063(1) | 15(1) |
| C(19) | -4462(1) | 2120(1) | 3979(1) | 16(1) |
| C(20) | -2230(2) | 3951(1) | 5051(1) | 25(1) |
| C(21) | -1193(1) | 3137(1) | 3307(1) | 24(1) |
| C(22) | -3705(2) | 930(1) | 1738(1) | 23(1) |
| C(23) | -6263(1) | 388(1) | 2548(1) | 22(1) |
| C(24) | -5395(1) | 2308(1) | 4574(1) | 23(1) |
| C(25) | -4371(1) | -1003(1) | 3451(1) | 16(1) |
| C(26) | -2908(1) | 876(1) | 5058(1) | 18(1) |
| C(27) | -1356(2) | -365(2) | 2773(1) | 34(1) |
| C(28) | 4(2) | -545(2) | 2757(1) | 29(1) |
| O(3) | -2774(1) | 1025(1) | 5800(1) | 27(1) |

| | | | | |
|---|---|---|---|---|
| O(4) | -5129(1) | -2029(1) | 3222(1) | 24(1) |
| Ru(2) | -3264(1) | 769(1) | 3834(1) | 11(1) |
| N(2) | -1474(1) | 233(1) | 3685(1) | 16(1) |
| B(1) | 8635(2) | 7388(2) | 4505(1) | 21(1) |
| F(1) | 9886(1) | 8155(1) | 4470(1) | 42(1) |
| F(2) | 7634(1) | 7864(1) | 4194(1) | 35(1) |
| F(3) | 8689(1) | 7480(1) | 5395(1) | 34(1) |
| F(4) | 8351(1) | 6107(1) | 3982(1) | 41(1) |
| B(2) | -1649(2) | 2561(2) | 8(1) | 21(1) |
| F(5) | -765(1) | 2361(1) | -517(1) | 51(1) |
| F(6) | -1886(1) | 3719(1) | 28(1) | 45(1) |
| F(7) | -2849(1) | 1543(1) | -323(1) | 43(1) |
| F(8) | -1050(1) | 2672(1) | 885(1) | 30(1) |

**Table B37:** Bond lengths [Å] and angles [°] for $[\eta^5\text{-}C_5(CH_3)_5Ru(CO)_2NH_2CH_2CH_3]BF_4$.

| | |
|---|---|
| C(1)-C(2) | 1.4290(17) |
| C(1)-C(5) | 1.4454(17) |
| C(1)-C(6) | 1.5008(16) |
| C(1)-Ru(1) | 2.2268(12) |
| C(2)-C(3) | 1.4260(16) |
| C(2)-C(7) | 1.4972(17) |
| C(2)-Ru(1) | 2.2715(11) |
| C(3)-C(4) | 1.4484(17) |
| C(3)-C(8) | 1.4993(17) |
| C(3)-Ru(1) | 2.2523(12) |
| C(4)-C(5) | 1.4291(17) |
| C(4)-C(9) | 1.5005(17) |
| C(4)-Ru(1) | 2.2144(12) |
| C(5)-C(10) | 1.4997(17) |
| C(5)-Ru(1) | 2.2153(12) |
| C(6)-H(6A) | 0.9800 |
| C(6)-H(6B) | 0.9800 |
| C(6)-H(6C) | 0.9800 |
| C(7)-H(7A) | 0.9800 |

| | |
|---|---|
| C(7)-H(7B) | 0.9800 |
| C(7)-H(7C) | 0.9800 |
| C(8)-H(8A) | 0.9800 |
| C(8)-H(8B) | 0.9800 |
| C(8)-H(8C) | 0.9800 |
| C(9)-H(9A) | 0.9800 |
| C(9)-H(9B) | 0.9800 |
| C(9)-H(9C) | 0.9800 |
| C(10)-H(10A) | 0.9800 |
| C(10)-H(10B) | 0.9800 |
| C(10)-H(10C) | 0.9800 |
| C(11)-O(1) | 1.1388(16) |
| C(11)-Ru(1) | 1.9047(13) |
| C(12)-O(2) | 1.1365(16) |
| C(12)-Ru(1) | 1.9043(13) |
| C(13)-N(1) | 1.4893(16) |
| C(13)-C(14) | 1.5148(18) |
| C(13)-H(13A) | 0.9900 |
| C(13)-H(13B) | 0.9900 |
| C(14)-H(14A) | 0.9800 |
| C(14)-H(14B) | 0.9800 |
| C(14)-H(14C) | 0.9800 |
| Ru(1)-N(1) | 2.1520(10) |
| N(1)-H(1A) | 0.9200 |
| N(1)-H(1B) | 0.9200 |
| C(15)-C(16) | 1.4212(17) |
| C(15)-C(19) | 1.4514(17) |
| C(15)-C(20) | 1.4991(17) |
| C(15)-Ru(2) | 2.2462(11) |
| C(16)-C(17) | 1.4447(17) |
| C(16)-C(21) | 1.4965(17) |
| C(16)-Ru(2) | 2.2686(12) |
| C(17)-C(18) | 1.4379(17) |
| C(17)-C(22) | 1.5036(17) |
| C(17)-Ru(2) | 2.2375(12) |
| C(18)-C(19) | 1.4314(17) |
| C(18)-C(23) | 1.5015(17) |
| C(18)-Ru(2) | 2.2231(12) |

| | |
|---|---|
| C(19)-C(24) | 1.4981(17) |
| C(19)-Ru(2) | 2.2156(12) |
| C(20)-H(20A) | 0.9800 |
| C(20)-H(20B) | 0.9800 |
| C(20)-H(20C) | 0.9800 |
| C(21)-H(21A) | 0.9800 |
| C(21)-H(21B) | 0.9800 |
| C(21)-H(21C) | 0.9800 |
| C(22)-H(22A) | 0.9800 |
| C(22)-H(22B) | 0.9800 |
| C(22)-H(22C) | 0.9800 |
| C(23)-H(23A) | 0.9800 |
| C(23)-H(23B) | 0.9800 |
| C(23)-H(23C) | 0.9800 |
| C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 |
| C(24)-H(24C) | 0.9800 |
| C(25)-O(4) | 1.1389(15) |
| C(25)-Ru(2) | 1.8972(12) |
| C(26)-O(3) | 1.1368(16) |
| C(26)-Ru(2) | 1.9059(13) |
| C(27)-N(2) | 1.4769(17) |
| C(27)-C(28) | 1.5051(19) |
| C(27)-H(27A) | 0.9900 |
| C(27)-H(27B) | 0.9900 |
| C(28)-H(28A) | 0.9800 |
| C(28)-H(28B) | 0.9800 |
| C(28)-H(28C) | 0.9800 |
| Ru(2)-N(2) | 2.1612(10) |
| N(2)-H(2A) | 0.9200 |
| N(2)-H(2B) | 0.9200 |
| B(1)-F(4) | 1.3813(18) |
| B(1)-F(2) | 1.3893(17) |
| B(1)-F(1) | 1.3948(17) |
| B(1)-F(3) | 1.3961(18) |
| B(2)-F(7) | 1.3708(17) |
| B(2)-F(5) | 1.3807(18) |
| B(2)-F(6) | 1.3903(17) |

| | |
|---|---|
| B(2)-F(8) | 1.4024(17) |
| | |
| C(2)-C(1)-C(5) | 107.57(10) |
| C(2)-C(1)-C(6) | 126.52(12) |
| C(5)-C(1)-C(6) | 125.41(12) |
| C(2)-C(1)-Ru(1) | 73.18(7) |
| C(5)-C(1)-Ru(1) | 70.58(7) |
| C(6)-C(1)-Ru(1) | 127.97(9) |
| C(3)-C(2)-C(1) | 108.82(10) |
| C(3)-C(2)-C(7) | 126.37(11) |
| C(1)-C(2)-C(7) | 124.78(11) |
| C(3)-C(2)-Ru(1) | 70.90(7) |
| C(1)-C(2)-Ru(1) | 69.79(7) |
| C(7)-C(2)-Ru(1) | 126.91(8) |
| C(2)-C(3)-C(4) | 107.64(10) |
| C(2)-C(3)-C(8) | 126.19(11) |
| C(4)-C(3)-C(8) | 125.65(11) |
| C(2)-C(3)-Ru(1) | 72.36(7) |
| C(4)-C(3)-Ru(1) | 69.67(7) |
| C(8)-C(3)-Ru(1) | 129.81(8) |
| C(5)-C(4)-C(3) | 107.87(10) |
| C(5)-C(4)-C(9) | 127.22(12) |
| C(3)-C(4)-C(9) | 124.64(11) |
| C(5)-C(4)-Ru(1) | 71.21(7) |
| C(3)-C(4)-Ru(1) | 72.50(7) |
| C(9)-C(4)-Ru(1) | 126.51(8) |
| C(4)-C(5)-C(1) | 108.05(10) |
| C(4)-C(5)-C(10) | 127.85(12) |
| C(1)-C(5)-C(10) | 123.91(12) |
| C(4)-C(5)-Ru(1) | 71.14(7) |
| C(1)-C(5)-Ru(1) | 71.44(7) |
| C(10)-C(5)-Ru(1) | 127.06(9) |
| C(1)-C(6)-H(6A) | 109.5 |
| C(1)-C(6)-H(6B) | 109.5 |
| H(6A)-C(6)-H(6B) | 109.5 |
| C(1)-C(6)-H(6C) | 109.5 |
| H(6A)-C(6)-H(6C) | 109.5 |
| H(6B)-C(6)-H(6C) | 109.5 |

| | |
|---|---|
| C(2)-C(7)-H(7A) | 109.5 |
| C(2)-C(7)-H(7B) | 109.5 |
| H(7A)-C(7)-H(7B) | 109.5 |
| C(2)-C(7)-H(7C) | 109.5 |
| H(7A)-C(7)-H(7C) | 109.5 |
| H(7B)-C(7)-H(7C) | 109.5 |
| C(3)-C(8)-H(8A) | 109.5 |
| C(3)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| C(3)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |
| C(4)-C(9)-H(9A) | 109.5 |
| C(4)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 109.5 |
| C(4)-C(9)-H(9C) | 109.5 |
| H(9A)-C(9)-H(9C) | 109.5 |
| H(9B)-C(9)-H(9C) | 109.5 |
| C(5)-C(10)-H(10A) | 109.5 |
| C(5)-C(10)-H(10B) | 109.5 |
| H(10A)-C(10)-H(10B) | 109.5 |
| C(5)-C(10)-H(10C) | 109.5 |
| H(10A)-C(10)-H(10C) | 109.5 |
| H(10B)-C(10)-H(10C) | 109.5 |
| O(1)-C(11)-Ru(1) | 174.97(11) |
| O(2)-C(12)-Ru(1) | 173.30(11) |
| N(1)-C(13)-C(14) | 111.99(11) |
| N(1)-C(13)-H(13A) | 109.2 |
| C(14)-C(13)-H(13A) | 109.2 |
| N(1)-C(13)-H(13B) | 109.2 |
| C(14)-C(13)-H(13B) | 109.2 |
| H(13A)-C(13)-H(13B) | 107.9 |
| C(13)-C(14)-H(14A) | 109.5 |
| C(13)-C(14)-H(14B) | 109.5 |
| H(14A)-C(14)-H(14B) | 109.5 |
| C(13)-C(14)-H(14C) | 109.5 |
| H(14A)-C(14)-H(14C) | 109.5 |
| H(14B)-C(14)-H(14C) | 109.5 |

| | |
|---|---|
| C(12)-Ru(1)-C(11) | 92.89(6) |
| C(12)-Ru(1)-N(1) | 90.35(5) |
| C(11)-Ru(1)-N(1) | 91.57(5) |
| C(12)-Ru(1)-C(4) | 118.84(5) |
| C(11)-Ru(1)-C(4) | 94.55(5) |
| N(1)-Ru(1)-C(4) | 149.72(4) |
| C(12)-Ru(1)-C(5) | 91.03(5) |
| C(11)-Ru(1)-C(5) | 123.28(5) |
| N(1)-Ru(1)-C(5) | 144.98(4) |
| C(4)-Ru(1)-C(5) | 37.64(4) |
| C(12)-Ru(1)-C(1) | 98.51(5) |
| C(11)-Ru(1)-C(1) | 157.71(5) |
| N(1)-Ru(1)-C(1) | 107.36(4) |
| C(4)-Ru(1)-C(1) | 63.17(4) |
| C(5)-Ru(1)-C(1) | 37.98(4) |
| C(12)-Ru(1)-C(3) | 153.72(5) |
| C(11)-Ru(1)-C(3) | 100.02(5) |
| N(1)-Ru(1)-C(3) | 111.89(4) |
| C(4)-Ru(1)-C(3) | 37.83(4) |
| C(5)-Ru(1)-C(3) | 62.75(4) |
| C(1)-Ru(1)-C(3) | 62.44(4) |
| C(12)-Ru(1)-C(2) | 133.49(5) |
| C(11)-Ru(1)-C(2) | 133.38(5) |
| N(1)-Ru(1)-C(2) | 92.44(4) |
| C(4)-Ru(1)-C(2) | 62.27(4) |
| C(5)-Ru(1)-C(2) | 62.23(4) |
| C(1)-Ru(1)-C(2) | 37.03(4) |
| C(3)-Ru(1)-C(2) | 36.75(4) |
| C(13)-N(1)-Ru(1) | 117.75(7) |
| C(13)-N(1)-H(1A) | 107.9 |
| Ru(1)-N(1)-H(1A) | 107.9 |
| C(13)-N(1)-H(1B) | 107.9 |
| Ru(1)-N(1)-H(1B) | 107.9 |
| H(1A)-N(1)-H(1B) | 107.2 |
| C(16)-C(15)-C(19) | 107.94(10) |
| C(16)-C(15)-C(20) | 126.08(11) |
| C(19)-C(15)-C(20) | 125.87(11) |
| C(16)-C(15)-Ru(2) | 72.51(7) |

| | |
|---|---|
| C(19)-C(15)-Ru(2) | 69.88(6) |
| C(20)-C(15)-Ru(2) | 126.26(9) |
| C(15)-C(16)-C(17) | 108.59(10) |
| C(15)-C(16)-C(21) | 125.31(12) |
| C(17)-C(16)-C(21) | 126.05(11) |
| C(15)-C(16)-Ru(2) | 70.80(7) |
| C(17)-C(16)-Ru(2) | 70.13(6) |
| C(21)-C(16)-Ru(2) | 126.90(9) |
| C(18)-C(17)-C(16) | 107.32(10) |
| C(18)-C(17)-C(22) | 125.30(11) |
| C(16)-C(17)-C(22) | 126.81(11) |
| C(18)-C(17)-Ru(2) | 70.65(7) |
| C(16)-C(17)-Ru(2) | 72.47(7) |
| C(22)-C(17)-Ru(2) | 128.96(8) |
| C(19)-C(18)-C(17) | 108.52(10) |
| C(19)-C(18)-C(23) | 125.91(11) |
| C(17)-C(18)-C(23) | 125.49(11) |
| C(19)-C(18)-Ru(2) | 70.90(7) |
| C(17)-C(18)-Ru(2) | 71.74(7) |
| C(23)-C(18)-Ru(2) | 125.71(8) |
| C(18)-C(19)-C(15) | 107.60(10) |
| C(18)-C(19)-C(24) | 126.04(11) |
| C(15)-C(19)-C(24) | 125.75(11) |
| C(18)-C(19)-Ru(2) | 71.47(7) |
| C(15)-C(19)-Ru(2) | 72.16(7) |
| C(24)-C(19)-Ru(2) | 128.79(9) |
| C(15)-C(20)-H(20A) | 109.5 |
| C(15)-C(20)-H(20B) | 109.5 |
| H(20A)-C(20)-H(20B) | 109.5 |
| C(15)-C(20)-H(20C) | 109.5 |
| H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 |
| C(16)-C(21)-H(21A) | 109.5 |
| C(16)-C(21)-H(21B) | 109.5 |
| H(21A)-C(21)-H(21B) | 109.5 |
| C(16)-C(21)-H(21C) | 109.5 |
| H(21A)-C(21)-H(21C) | 109.5 |
| H(21B)-C(21)-H(21C) | 109.5 |

| | |
|---|---|
| C(17)-C(22)-H(22A) | 109.5 |
| C(17)-C(22)-H(22B) | 109.5 |
| H(22A)-C(22)-H(22B) | 109.5 |
| C(17)-C(22)-H(22C) | 109.5 |
| H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 |
| C(18)-C(23)-H(23A) | 109.5 |
| C(18)-C(23)-H(23B) | 109.5 |
| H(23A)-C(23)-H(23B) | 109.5 |
| C(18)-C(23)-H(23C) | 109.5 |
| H(23A)-C(23)-H(23C) | 109.5 |
| H(23B)-C(23)-H(23C) | 109.5 |
| C(19)-C(24)-H(24A) | 109.5 |
| C(19)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| C(19)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |
| O(4)-C(25)-Ru(2) | 174.10(11) |
| O(3)-C(26)-Ru(2) | 172.85(11) |
| N(2)-C(27)-C(28) | 113.28(12) |
| N(2)-C(27)-H(27A) | 108.9 |
| C(28)-C(27)-H(27A) | 108.9 |
| N(2)-C(27)-H(27B) | 108.9 |
| C(28)-C(27)-H(27B) | 108.9 |
| H(27A)-C(27)-H(27B) | 107.7 |
| C(27)-C(28)-H(28A) | 109.5 |
| C(27)-C(28)-H(28B) | 109.5 |
| H(28A)-C(28)-H(28B) | 109.5 |
| C(27)-C(28)-H(28C) | 109.5 |
| H(28A)-C(28)-H(28C) | 109.5 |
| H(28B)-C(28)-H(28C) | 109.5 |
| C(25)-Ru(2)-C(26) | 91.93(5) |
| C(25)-Ru(2)-N(2) | 91.72(4) |
| C(26)-Ru(2)-N(2) | 91.40(5) |
| C(25)-Ru(2)-C(19) | 112.66(5) |
| C(26)-Ru(2)-C(19) | 95.27(5) |
| N(2)-Ru(2)-C(19) | 154.41(4) |

| | |
|---|---|
| C(25)-Ru(2)-C(18) | 92.20(5) |
| C(26)-Ru(2)-C(18) | 128.93(5) |
| N(2)-Ru(2)-C(18) | 139.28(4) |
| C(19)-Ru(2)-C(18) | 37.63(4) |
| C(25)-Ru(2)-C(17) | 107.61(5) |
| C(26)-Ru(2)-C(17) | 154.92(5) |
| N(2)-Ru(2)-C(17) | 103.27(4) |
| C(19)-Ru(2)-C(17) | 63.06(4) |
| C(18)-Ru(2)-C(17) | 37.61(4) |
| C(25)-Ru(2)-C(15) | 150.58(5) |
| C(26)-Ru(2)-C(15) | 92.73(5) |
| N(2)-Ru(2)-C(15) | 117.17(4) |
| C(19)-Ru(2)-C(15) | 37.96(4) |
| C(18)-Ru(2)-C(15) | 62.73(4) |
| C(17)-Ru(2)-C(15) | 62.54(4) |
| C(25)-Ru(2)-C(16) | 144.69(5) |
| C(26)-Ru(2)-C(16) | 122.82(5) |
| N(2)-Ru(2)-C(16) | 93.34(4) |
| C(19)-Ru(2)-C(16) | 62.39(4) |
| C(18)-Ru(2)-C(16) | 62.24(4) |
| C(17)-Ru(2)-C(16) | 37.39(4) |
| C(15)-Ru(2)-C(16) | 36.69(4) |
| C(27)-N(2)-Ru(2) | 118.62(8) |
| C(27)-N(2)-H(2A) | 107.7 |
| Ru(2)-N(2)-H(2A) | 107.7 |
| C(27)-N(2)-H(2B) | 107.7 |
| Ru(2)-N(2)-H(2B) | 107.7 |
| H(2A)-N(2)-H(2B) | 107.1 |
| F(4)-B(1)-F(2) | 109.83(12) |
| F(4)-B(1)-F(1) | 110.31(13) |
| F(2)-B(1)-F(1) | 108.53(12) |
| F(4)-B(1)-F(3) | 110.14(12) |
| F(2)-B(1)-F(3) | 109.39(12) |
| F(1)-B(1)-F(3) | 108.61(11) |
| F(7)-B(2)-F(5) | 110.52(13) |
| F(7)-B(2)-F(6) | 110.15(12) |
| F(5)-B(2)-F(6) | 108.98(12) |
| F(7)-B(2)-F(8) | 109.45(12) |

| | |
|---|---|
| F(5)-B(2)-F(8) | 109.18(12) |
| F(6)-B(2)-F(8) | 108.52(12) |

**Table B38:** Anisotropic displacement parameters ($Å^2 x\ 10^3$)for [$\eta^5$-$C_5(CH_3)_5Ru(CO)_2NH_2CH_2CH_3]BF_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 15(1) | 13(1) | 17(1) | 5(1) | 1(1) | 4(1) |
| C(2) | 16(1) | 15(1) | 17(1) | 8(1) | 5(1) | 6(1) |
| C(3) | 16(1) | 13(1) | 14(1) | 5(1) | 2(1) | 5(1) |
| C(4) | 14(1) | 17(1) | 19(1) | 9(1) | 4(1) | 6(1) |
| C(5) | 20(1) | 18(1) | 15(1) | 6(1) | 4(1) | 10(1) |
| C(6) | 21(1) | 16(1) | 29(1) | 4(1) | -5(1) | 0(1) |
| C(7) | 24(1) | 28(1) | 28(1) | 15(1) | 15(1) | 11(1) |
| C(8) | 28(1) | 17(1) | 18(1) | 2(1) | -3(1) | 6(1) |
| C(9) | 14(1) | 29(1) | 39(1) | 20(1) | 9(1) | 7(1) |
| C(10) | 39(1) | 30(1) | 17(1) | 7(1) | 10(1) | 23(1) |
| C(11) | 18(1) | 22(1) | 22(1) | 10(1) | 7(1) | 9(1) |
| C(12) | 20(1) | 21(1) | 20(1) | 9(1) | 6(1) | 11(1) |
| C(13) | 19(1) | 19(1) | 21(1) | 2(1) | 3(1) | 8(1) |
| C(14) | 24(1) | 27(1) | 30(1) | 4(1) | 11(1) | 13(1) |
| O(1) | 27(1) | 24(1) | 39(1) | 15(1) | 11(1) | 2(1) |
| O(2) | 32(1) | 36(1) | 17(1) | 9(1) | 6(1) | 16(1) |
| Ru(1) | 11(1) | 13(1) | 12(1) | 5(1) | 3(1) | 4(1) |
| N(1) | 14(1) | 17(1) | 16(1) | 5(1) | 4(1) | 6(1) |
| C(15) | 20(1) | 12(1) | 17(1) | 4(1) | 5(1) | 5(1) |
| C(16) | 18(1) | 14(1) | 21(1) | 8(1) | 7(1) | 6(1) |
| C(17) | 19(1) | 17(1) | 14(1) | 7(1) | 6(1) | 9(1) |
| C(18) | 16(1) | 15(1) | 16(1) | 7(1) | 4(1) | 7(1) |
| C(19) | 19(1) | 14(1) | 17(1) | 7(1) | 7(1) | 8(1) |
| C(20) | 31(1) | 16(1) | 21(1) | 0(1) | 2(1) | 4(1) |
| C(21) | 19(1) | 22(1) | 34(1) | 13(1) | 12(1) | 5(1) |
| C(22) | 32(1) | 26(1) | 15(1) | 7(1) | 9(1) | 15(1) |
| C(23) | 17(1) | 22(1) | 24(1) | 9(1) | 0(1) | 5(1) |
| C(24) | 27(1) | 24(1) | 26(1) | 11(1) | 16(1) | 13(1) |
| C(25) | 15(1) | 18(1) | 17(1) | 7(1) | 3(1) | 7(1) |
| C(26) | 16(1) | 17(1) | 19(1) | 7(1) | 4(1) | 5(1) |
| C(27) | 30(1) | 56(1) | 20(1) | 6(1) | 8(1) | 27(1) |
| C(28) | 28(1) | 29(1) | 38(1) | 12(1) | 18(1) | 16(1) |
| O(3) | 29(1) | 34(1) | 17(1) | 11(1) | 6(1) | 7(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O(4) | 20(1) | 16(1) | 30(1) | 6(1) | 1(1) | 2(1) |
| Ru(2) | 12(1) | 11(1) | 11(1) | 3(1) | 3(1) | 3(1) |
| N(2) | 15(1) | 16(1) | 17(1) | 6(1) | 4(1) | 6(1) |
| B(1) | 17(1) | 24(1) | 22(1) | 8(1) | 2(1) | 5(1) |
| F(1) | 20(1) | 61(1) | 28(1) | 8(1) | 5(1) | -7(1) |
| F(2) | 28(1) | 33(1) | 48(1) | 23(1) | 2(1) | 12(1) |
| F(3) | 36(1) | 42(1) | 25(1) | 16(1) | 8(1) | 10(1) |
| F(4) | 48(1) | 29(1) | 41(1) | 4(1) | 7(1) | 17(1) |
| B(2) | 19(1) | 22(1) | 22(1) | 8(1) | 5(1) | 7(1) |
| F(5) | 45(1) | 79(1) | 50(1) | 30(1) | 33(1) | 33(1) |
| F(6) | 79(1) | 35(1) | 37(1) | 21(1) | 19(1) | 34(1) |
| F(7) | 29(1) | 42(1) | 37(1) | 6(1) | -4(1) | -7(1) |
| F(8) | 26(1) | 34(1) | 28(1) | 16(1) | -1(1) | 4(1) |

**Table B39:** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for [$\eta^5$-$C_5(CH_3)_5Ru(CO)_2NH_2CH_2CH_3]BF_4$.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(6A) | 1431 | 345 | 860 | 38 |
| H(6B) | 1291 | 914 | 56 | 38 |
| H(6C) | 570 | 1312 | 840 | 38 |
| H(7A) | 1866 | 2521 | 2969 | 36 |
| H(7B) | 907 | 2820 | 2229 | 36 |
| H(7C) | 2005 | 3995 | 3051 | 36 |
| H(8A) | 4234 | 5282 | 3570 | 35 |
| H(8B) | 5571 | 5747 | 3241 | 35 |
| H(8C) | 5384 | 4611 | 3667 | 35 |
| H(9A) | 6886 | 3852 | 2089 | 38 |
| H(9B) | 6631 | 5163 | 2030 | 38 |
| H(9C) | 6492 | 4021 | 1135 | 38 |
| H(10A) | 5019 | 2150 | 64 | 40 |
| H(10B) | 3418 | 1616 | -391 | 40 |
| H(10C) | 4080 | 862 | 169 | 40 |
| H(13A) | 2263 | 6834 | 2146 | 24 |

| | | | | |
|---|---|---|---|---|
| H(13B) | 2184 | 5802 | 2661 | 24 |
| H(14A) | -102 | 6363 | 1850 | 41 |
| H(14B) | 516 | 6766 | 2905 | 41 |
| H(14C) | -227 | 5264 | 2309 | 41 |
| H(1A) | 1288 | 5248 | 841 | 19 |
| H(1B) | 769 | 4248 | 1243 | 19 |
| H(20A) | -1270 | 4009 | 5145 | 38 |
| H(20B) | -2568 | 3751 | 5545 | 38 |
| H(20C) | -2320 | 4783 | 5031 | 38 |
| H(21A) | -1061 | 4048 | 3359 | 36 |
| H(21B) | -1104 | 2663 | 2721 | 36 |
| H(21C) | -505 | 3100 | 3781 | 36 |
| H(22A) | -4336 | 34 | 1491 | 34 |
| H(22B) | -2789 | 928 | 1697 | 34 |
| H(22C) | -4000 | 1448 | 1396 | 34 |
| H(23A) | -6721 | 29 | 2949 | 33 |
| H(23B) | -6206 | -325 | 2059 | 33 |
| H(23C) | -6779 | 870 | 2300 | 33 |
| H(24A) | -5671 | 3063 | 4553 | 34 |
| H(24B) | -4922 | 2455 | 5190 | 34 |
| H(24C) | -6202 | 1528 | 4368 | 34 |
| H(27A) | -1508 | 192 | 2414 | 41 |
| H(27B) | -2077 | -1223 | 2486 | 41 |
| H(28A) | 724 | 302 | 3034 | 44 |
| H(28B) | 25 | -932 | 2136 | 44 |
| H(28C) | 148 | -1123 | 3092 | 44 |
| H(2A) | -728 | 971 | 3968 | 19 |
| H(2B) | -1418 | -337 | 3990 | 19 |

**Table B40:** Torsion angles [°] for $[\eta^5\text{-}C_5(CH_3)_5Ru(CO)_2NH_2CH_2CH_3]BF_4$.

| | |
|---|---|
| C(5)-C(1)-C(2)-C(3) | 2.21(13) |
| C(6)-C(1)-C(2)-C(3) | 174.43(11) |
| Ru(1)-C(1)-C(2)-C(3) | -60.40(8) |
| C(5)-C(1)-C(2)-C(7) | -175.82(11) |
| C(6)-C(1)-C(2)-C(7) | -3.60(19) |
| Ru(1)-C(1)-C(2)-C(7) | 121.57(12) |
| C(5)-C(1)-C(2)-Ru(1) | 62.61(8) |
| C(6)-C(1)-C(2)-Ru(1) | -125.17(12) |
| C(1)-C(2)-C(3)-C(4) | -1.36(13) |
| C(7)-C(2)-C(3)-C(4) | 176.63(11) |
| Ru(1)-C(2)-C(3)-C(4) | -61.07(8) |
| C(1)-C(2)-C(3)-C(8) | -173.43(11) |
| C(7)-C(2)-C(3)-C(8) | 4.56(19) |
| Ru(1)-C(2)-C(3)-C(8) | 126.86(12) |
| C(1)-C(2)-C(3)-Ru(1) | 59.71(8) |
| C(7)-C(2)-C(3)-Ru(1) | -122.30(12) |
| C(2)-C(3)-C(4)-C(5) | -0.03(13) |
| C(8)-C(3)-C(4)-C(5) | 172.10(11) |
| Ru(1)-C(3)-C(4)-C(5) | -62.84(8) |
| C(2)-C(3)-C(4)-C(9) | -174.48(11) |
| C(8)-C(3)-C(4)-C(9) | -2.35(19) |
| Ru(1)-C(3)-C(4)-C(9) | 122.71(12) |
| C(2)-C(3)-C(4)-Ru(1) | 62.81(8) |
| C(8)-C(3)-C(4)-Ru(1) | -125.06(12) |
| C(3)-C(4)-C(5)-C(1) | 1.39(13) |
| C(9)-C(4)-C(5)-C(1) | 175.65(11) |
| Ru(1)-C(4)-C(5)-C(1) | -62.29(8) |
| C(3)-C(4)-C(5)-C(10) | -173.56(12) |
| C(9)-C(4)-C(5)-C(10) | 0.7(2) |
| Ru(1)-C(4)-C(5)-C(10) | 122.76(13) |
| C(3)-C(4)-C(5)-Ru(1) | 63.68(8) |
| C(9)-C(4)-C(5)-Ru(1) | -122.06(12) |
| C(2)-C(1)-C(5)-C(4) | -2.22(13) |
| C(6)-C(1)-C(5)-C(4) | -174.55(11) |
| Ru(1)-C(1)-C(5)-C(4) | 62.10(8) |
| C(2)-C(1)-C(5)-C(10) | 172.97(11) |

| | |
|---|---|
| C(6)-C(1)-C(5)-C(10) | 0.64(19) |
| Ru(1)-C(1)-C(5)-C(10) | -122.71(12) |
| C(2)-C(1)-C(5)-Ru(1) | -64.32(8) |
| C(6)-C(1)-C(5)-Ru(1) | 123.35(12) |
| O(2)-C(12)-Ru(1)-C(11) | 118.2(10) |
| O(2)-C(12)-Ru(1)-N(1) | -150.2(10) |
| O(2)-C(12)-Ru(1)-C(4) | 21.4(10) |
| O(2)-C(12)-Ru(1)-C(5) | -5.2(10) |
| O(2)-C(12)-Ru(1)-C(1) | -42.5(10) |
| O(2)-C(12)-Ru(1)-C(3) | -1.5(11) |
| O(2)-C(12)-Ru(1)-C(2) | -56.5(10) |
| O(1)-C(11)-Ru(1)-C(12) | -107.1(14) |
| O(1)-C(11)-Ru(1)-N(1) | 162.5(14) |
| O(1)-C(11)-Ru(1)-C(4) | 12.1(14) |
| O(1)-C(11)-Ru(1)-C(5) | -14.0(14) |
| O(1)-C(11)-Ru(1)-C(1) | 13.8(15) |
| O(1)-C(11)-Ru(1)-C(3) | 49.9(14) |
| O(1)-C(11)-Ru(1)-C(2) | 67.6(14) |
| C(5)-C(4)-Ru(1)-C(12) | -47.12(9) |
| C(3)-C(4)-Ru(1)-C(12) | -163.69(7) |
| C(9)-C(4)-Ru(1)-C(12) | 75.77(13) |
| C(5)-C(4)-Ru(1)-C(11) | -142.95(8) |
| C(3)-C(4)-Ru(1)-C(11) | 100.48(7) |
| C(9)-C(4)-Ru(1)-C(11) | -20.06(12) |
| C(5)-C(4)-Ru(1)-N(1) | 116.04(9) |
| C(3)-C(4)-Ru(1)-N(1) | -0.52(12) |
| C(9)-C(4)-Ru(1)-N(1) | -121.07(12) |
| C(3)-C(4)-Ru(1)-C(5) | -116.56(10) |
| C(9)-C(4)-Ru(1)-C(5) | 122.89(15) |
| C(5)-C(4)-Ru(1)-C(1) | 37.76(7) |
| C(3)-C(4)-Ru(1)-C(1) | -78.81(7) |
| C(9)-C(4)-Ru(1)-C(1) | 160.64(13) |
| C(5)-C(4)-Ru(1)-C(3) | 116.56(10) |
| C(9)-C(4)-Ru(1)-C(3) | -120.55(14) |
| C(5)-C(4)-Ru(1)-C(2) | 79.61(7) |
| C(3)-C(4)-Ru(1)-C(2) | -36.95(6) |
| C(9)-C(4)-Ru(1)-C(2) | -157.50(13) |
| C(4)-C(5)-Ru(1)-C(12) | 140.06(8) |

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|---|---|
| C(1)-C(5)-Ru(1)-C(12) | -102.56(7) |
| C(10)-C(5)-Ru(1)-C(12) | 16.38(12) |
| C(4)-C(5)-Ru(1)-C(11) | 45.92(9) |
| C(1)-C(5)-Ru(1)-C(11) | 163.31(7) |
| C(10)-C(5)-Ru(1)-C(11) | -77.76(13) |
| C(4)-C(5)-Ru(1)-N(1) | -127.85(8) |
| C(1)-C(5)-Ru(1)-N(1) | -10.47(11) |
| C(10)-C(5)-Ru(1)-N(1) | 108.47(12) |
| C(1)-C(5)-Ru(1)-C(4) | 117.38(10) |
| C(10)-C(5)-Ru(1)-C(4) | -123.68(15) |
| C(4)-C(5)-Ru(1)-C(1) | -117.38(10) |
| C(10)-C(5)-Ru(1)-C(1) | 118.94(14) |
| C(4)-C(5)-Ru(1)-C(3) | -38.10(7) |
| C(1)-C(5)-Ru(1)-C(3) | 79.28(7) |
| C(10)-C(5)-Ru(1)-C(3) | -161.78(13) |
| C(4)-C(5)-Ru(1)-C(2) | -79.73(7) |
| C(1)-C(5)-Ru(1)-C(2) | 37.65(7) |
| C(10)-C(5)-Ru(1)-C(2) | 156.59(13) |
| C(2)-C(1)-Ru(1)-C(12) | -163.16(7) |
| C(5)-C(1)-Ru(1)-C(12) | 80.67(7) |
| C(6)-C(1)-Ru(1)-C(12) | -39.60(12) |
| C(2)-C(1)-Ru(1)-C(11) | 76.88(15) |
| C(5)-C(1)-Ru(1)-C(11) | -39.29(16) |
| C(6)-C(1)-Ru(1)-C(11) | -159.56(13) |
| C(2)-C(1)-Ru(1)-N(1) | -70.11(7) |
| C(5)-C(1)-Ru(1)-N(1) | 173.73(7) |
| C(6)-C(1)-Ru(1)-N(1) | 53.45(12) |
| C(2)-C(1)-Ru(1)-C(4) | 78.74(7) |
| C(5)-C(1)-Ru(1)-C(4) | -37.43(7) |
| C(6)-C(1)-Ru(1)-C(4) | -157.70(13) |
| C(2)-C(1)-Ru(1)-C(5) | 116.16(10) |
| C(6)-C(1)-Ru(1)-C(5) | -120.28(15) |
| C(2)-C(1)-Ru(1)-C(3) | 36.00(7) |
| C(5)-C(1)-Ru(1)-C(3) | -80.17(7) |
| C(6)-C(1)-Ru(1)-C(3) | 159.56(13) |
| C(5)-C(1)-Ru(1)-C(2) | -116.16(10) |
| C(6)-C(1)-Ru(1)-C(2) | 123.56(15) |
| C(2)-C(3)-Ru(1)-C(12) | -83.43(13) |

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|---|---|
| C(4)-C(3)-Ru(1)-C(12) | 33.76(14) |
| C(8)-C(3)-Ru(1)-C(12) | 153.78(12) |
| C(2)-C(3)-Ru(1)-C(11) | 158.32(7) |
| C(4)-C(3)-Ru(1)-C(11) | -84.49(7) |
| C(8)-C(3)-Ru(1)-C(11) | 35.54(12) |
| C(2)-C(3)-Ru(1)-N(1) | 62.53(7) |
| C(4)-C(3)-Ru(1)-N(1) | 179.72(6) |
| C(8)-C(3)-Ru(1)-N(1) | -60.26(12) |
| C(2)-C(3)-Ru(1)-C(4) | -117.19(10) |
| C(8)-C(3)-Ru(1)-C(4) | 120.02(14) |
| C(2)-C(3)-Ru(1)-C(5) | -79.28(7) |
| C(4)-C(3)-Ru(1)-C(5) | 37.92(7) |
| C(8)-C(3)-Ru(1)-C(5) | 157.94(13) |
| C(2)-C(3)-Ru(1)-C(1) | -36.28(7) |
| C(4)-C(3)-Ru(1)-C(1) | 80.91(7) |
| C(8)-C(3)-Ru(1)-C(1) | -159.06(13) |
| C(4)-C(3)-Ru(1)-C(2) | 117.19(10) |
| C(8)-C(3)-Ru(1)-C(2) | -122.78(15) |
| C(3)-C(2)-Ru(1)-C(12) | 142.68(8) |
| C(1)-C(2)-Ru(1)-C(12) | 23.26(10) |
| C(7)-C(2)-Ru(1)-C(12) | -95.67(12) |
| C(3)-C(2)-Ru(1)-C(11) | -30.03(10) |
| C(1)-C(2)-Ru(1)-C(11) | -149.46(8) |
| C(7)-C(2)-Ru(1)-C(11) | 91.62(12) |
| C(3)-C(2)-Ru(1)-N(1) | -124.51(7) |
| C(1)-C(2)-Ru(1)-N(1) | 116.06(7) |
| C(7)-C(2)-Ru(1)-N(1) | -2.87(11) |
| C(3)-C(2)-Ru(1)-C(4) | 38.05(7) |
| C(1)-C(2)-Ru(1)-C(4) | -81.38(7) |
| C(7)-C(2)-Ru(1)-C(4) | 159.69(13) |
| C(3)-C(2)-Ru(1)-C(5) | 80.81(7) |
| C(1)-C(2)-Ru(1)-C(5) | -38.62(7) |
| C(7)-C(2)-Ru(1)-C(5) | -157.55(12) |
| C(3)-C(2)-Ru(1)-C(1) | 119.43(10) |
| C(7)-C(2)-Ru(1)-C(1) | -118.93(14) |
| C(1)-C(2)-Ru(1)-C(3) | -119.43(10) |
| C(7)-C(2)-Ru(1)-C(3) | 121.65(14) |
| C(14)-C(13)-N(1)-Ru(1) | -162.48(9) |

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|---|---|
| C(12)-Ru(1)-N(1)-C(13) | -152.90(9) |
| C(11)-Ru(1)-N(1)-C(13) | -60.00(9) |
| C(4)-Ru(1)-N(1)-C(13) | 41.79(13) |
| C(5)-Ru(1)-N(1)-C(13) | 114.80(10) |
| C(1)-Ru(1)-N(1)-C(13) | 108.07(9) |
| C(3)-Ru(1)-N(1)-C(13) | 41.45(10) |
| C(2)-Ru(1)-N(1)-C(13) | 73.54(9) |
| C(19)-C(15)-C(16)-C(17) | -1.03(13) |
| C(20)-C(15)-C(16)-C(17) | -177.26(12) |
| Ru(2)-C(15)-C(16)-C(17) | 60.21(8) |
| C(19)-C(15)-C(16)-C(21) | 176.59(11) |
| C(20)-C(15)-C(16)-C(21) | 0.4(2) |
| Ru(2)-C(15)-C(16)-C(21) | -122.17(12) |
| C(19)-C(15)-C(16)-Ru(2) | -61.24(8) |
| C(20)-C(15)-C(16)-Ru(2) | 122.52(12) |
| C(15)-C(16)-C(17)-C(18) | 1.83(13) |
| C(21)-C(16)-C(17)-C(18) | -175.76(11) |
| Ru(2)-C(16)-C(17)-C(18) | 62.46(8) |
| C(15)-C(16)-C(17)-C(22) | 173.42(11) |
| C(21)-C(16)-C(17)-C(22) | -4.2(2) |
| Ru(2)-C(16)-C(17)-C(22) | -125.96(12) |
| C(15)-C(16)-C(17)-Ru(2) | -60.63(8) |
| C(21)-C(16)-C(17)-Ru(2) | 121.78(12) |
| C(16)-C(17)-C(18)-C(19) | -1.94(13) |
| C(22)-C(17)-C(18)-C(19) | -173.69(11) |
| Ru(2)-C(17)-C(18)-C(19) | 61.71(8) |
| C(16)-C(17)-C(18)-C(23) | 175.04(11) |
| C(22)-C(17)-C(18)-C(23) | 3.29(19) |
| Ru(2)-C(17)-C(18)-C(23) | -121.31(12) |
| C(16)-C(17)-C(18)-Ru(2) | -63.65(8) |
| C(22)-C(17)-C(18)-Ru(2) | 124.60(12) |
| C(17)-C(18)-C(19)-C(15) | 1.32(13) |
| C(23)-C(18)-C(19)-C(15) | -175.65(11) |
| Ru(2)-C(18)-C(19)-C(15) | 63.56(8) |
| C(17)-C(18)-C(19)-C(24) | 172.78(11) |
| C(23)-C(18)-C(19)-C(24) | -4.18(19) |
| Ru(2)-C(18)-C(19)-C(24) | -124.98(12) |
| C(17)-C(18)-C(19)-Ru(2) | -62.24(8) |

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|---|---|
| C(23)-C(18)-C(19)-Ru(2) | 120.79(12) |
| C(16)-C(15)-C(19)-C(18) | -0.18(13) |
| C(20)-C(15)-C(19)-C(18) | 176.07(11) |
| Ru(2)-C(15)-C(19)-C(18) | -63.11(8) |
| C(16)-C(15)-C(19)-C(24) | -171.67(11) |
| C(20)-C(15)-C(19)-C(24) | 4.6(2) |
| Ru(2)-C(15)-C(19)-C(24) | 125.40(12) |
| C(16)-C(15)-C(19)-Ru(2) | 62.93(8) |
| C(20)-C(15)-C(19)-Ru(2) | -120.82(12) |
| O(4)-C(25)-Ru(2)-C(26) | 94.9(11) |
| O(4)-C(25)-Ru(2)-N(2) | -173.6(11) |
| O(4)-C(25)-Ru(2)-C(19) | -1.6(11) |
| O(4)-C(25)-Ru(2)-C(18) | -34.2(11) |
| O(4)-C(25)-Ru(2)-C(17) | -69.1(11) |
| O(4)-C(25)-Ru(2)-C(15) | -4.1(11) |
| O(4)-C(25)-Ru(2)-C(16) | -75.4(11) |
| O(3)-C(26)-Ru(2)-C(25) | -111.7(9) |
| O(3)-C(26)-Ru(2)-N(2) | 156.6(9) |
| O(3)-C(26)-Ru(2)-C(19) | 1.3(9) |
| O(3)-C(26)-Ru(2)-C(18) | -17.3(9) |
| O(3)-C(26)-Ru(2)-C(17) | 30.2(10) |
| O(3)-C(26)-Ru(2)-C(15) | 39.3(9) |
| O(3)-C(26)-Ru(2)-C(16) | 61.7(9) |
| C(18)-C(19)-Ru(2)-C(25) | -61.73(8) |
| C(15)-C(19)-Ru(2)-C(25) | -178.01(7) |
| C(24)-C(19)-Ru(2)-C(25) | 60.06(12) |
| C(18)-C(19)-Ru(2)-C(26) | -156.05(7) |
| C(15)-C(19)-Ru(2)-C(26) | 87.67(7) |
| C(24)-C(19)-Ru(2)-C(26) | -34.26(12) |
| C(18)-C(19)-Ru(2)-N(2) | 99.52(11) |
| C(15)-C(19)-Ru(2)-N(2) | -16.77(13) |
| C(24)-C(19)-Ru(2)-N(2) | -138.69(11) |
| C(15)-C(19)-Ru(2)-C(18) | -116.28(10) |
| C(24)-C(19)-Ru(2)-C(18) | 121.79(14) |
| C(18)-C(19)-Ru(2)-C(17) | 37.22(7) |
| C(15)-C(19)-Ru(2)-C(17) | -79.07(7) |
| C(24)-C(19)-Ru(2)-C(17) | 159.01(13) |
| C(18)-C(19)-Ru(2)-C(15) | 116.28(10) |

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|---|---|
| C(24)-C(19)-Ru(2)-C(15) | -121.93(14) |
| C(18)-C(19)-Ru(2)-C(16) | 79.49(7) |
| C(15)-C(19)-Ru(2)-C(16) | -36.79(7) |
| C(24)-C(19)-Ru(2)-C(16) | -158.72(13) |
| C(19)-C(18)-Ru(2)-C(25) | 125.58(7) |
| C(17)-C(18)-Ru(2)-C(25) | -116.50(7) |
| C(23)-C(18)-Ru(2)-C(25) | 4.55(11) |
| C(19)-C(18)-Ru(2)-C(26) | 31.31(9) |
| C(17)-C(18)-Ru(2)-C(26) | 149.23(7) |
| C(23)-C(18)-Ru(2)-C(26) | -89.72(12) |
| C(19)-C(18)-Ru(2)-N(2) | -139.23(7) |
| C(17)-C(18)-Ru(2)-N(2) | -21.31(10) |
| C(23)-C(18)-Ru(2)-N(2) | 99.74(11) |
| C(17)-C(18)-Ru(2)-C(19) | 117.92(10) |
| C(23)-C(18)-Ru(2)-C(19) | -121.03(14) |
| C(19)-C(18)-Ru(2)-C(17) | -117.92(10) |
| C(23)-C(18)-Ru(2)-C(17) | 121.05(14) |
| C(19)-C(18)-Ru(2)-C(15) | -38.35(7) |
| C(17)-C(18)-Ru(2)-C(15) | 79.57(7) |
| C(23)-C(18)-Ru(2)-C(15) | -159.38(12) |
| C(19)-C(18)-Ru(2)-C(16) | -79.92(7) |
| C(17)-C(18)-Ru(2)-C(16) | 38.00(7) |
| C(23)-C(18)-Ru(2)-C(16) | 159.05(12) |
| C(18)-C(17)-Ru(2)-C(25) | 69.75(8) |
| C(16)-C(17)-Ru(2)-C(25) | -174.03(7) |
| C(22)-C(17)-Ru(2)-C(25) | -50.49(12) |
| C(18)-C(17)-Ru(2)-C(26) | -69.84(13) |
| C(16)-C(17)-Ru(2)-C(26) | 46.37(14) |
| C(22)-C(17)-Ru(2)-C(26) | 169.92(11) |
| C(18)-C(17)-Ru(2)-N(2) | 165.90(7) |
| C(16)-C(17)-Ru(2)-N(2) | -77.88(7) |
| C(22)-C(17)-Ru(2)-N(2) | 45.66(12) |
| C(18)-C(17)-Ru(2)-C(19) | -37.24(7) |
| C(16)-C(17)-Ru(2)-C(19) | 78.98(7) |
| C(22)-C(17)-Ru(2)-C(19) | -157.47(13) |
| C(16)-C(17)-Ru(2)-C(18) | 116.21(10) |
| C(22)-C(17)-Ru(2)-C(18) | -120.24(14) |
| C(18)-C(17)-Ru(2)-C(15) | -80.13(7) |

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|---|---|
| C(16)-C(17)-Ru(2)-C(15) | 36.09(7) |
| C(22)-C(17)-Ru(2)-C(15) | 159.63(13) |
| C(18)-C(17)-Ru(2)-C(16) | -116.21(10) |
| C(22)-C(17)-Ru(2)-C(16) | 123.55(14) |
| C(16)-C(15)-Ru(2)-C(25) | -113.61(11) |
| C(19)-C(15)-Ru(2)-C(25) | 3.73(13) |
| C(20)-C(15)-Ru(2)-C(25) | 124.07(12) |
| C(16)-C(15)-Ru(2)-C(26) | 147.58(8) |
| C(19)-C(15)-Ru(2)-C(26) | -95.08(7) |
| C(20)-C(15)-Ru(2)-C(26) | 25.26(12) |
| C(16)-C(15)-Ru(2)-N(2) | 54.60(8) |
| C(19)-C(15)-Ru(2)-N(2) | 171.95(6) |
| C(20)-C(15)-Ru(2)-N(2) | -67.71(12) |
| C(16)-C(15)-Ru(2)-C(19) | -117.34(10) |
| C(20)-C(15)-Ru(2)-C(19) | 120.34(14) |
| C(16)-C(15)-Ru(2)-C(18) | -79.33(8) |
| C(19)-C(15)-Ru(2)-C(18) | 38.01(7) |
| C(20)-C(15)-Ru(2)-C(18) | 158.35(13) |
| C(16)-C(15)-Ru(2)-C(17) | -36.77(7) |
| C(19)-C(15)-Ru(2)-C(17) | 80.57(7) |
| C(20)-C(15)-Ru(2)-C(17) | -159.08(13) |
| C(19)-C(15)-Ru(2)-C(16) | 117.34(10) |
| C(20)-C(15)-Ru(2)-C(16) | -122.31(14) |
| C(15)-C(16)-Ru(2)-C(25) | 128.87(9) |
| C(17)-C(16)-Ru(2)-C(25) | 9.87(12) |
| C(21)-C(16)-Ru(2)-C(25) | -110.88(12) |
| C(15)-C(16)-Ru(2)-C(26) | -39.59(9) |
| C(17)-C(16)-Ru(2)-C(26) | -158.59(7) |
| C(21)-C(16)-Ru(2)-C(26) | 80.67(12) |
| C(15)-C(16)-Ru(2)-N(2) | -133.41(7) |
| C(17)-C(16)-Ru(2)-N(2) | 107.59(7) |
| C(21)-C(16)-Ru(2)-N(2) | -13.16(12) |
| C(15)-C(16)-Ru(2)-C(19) | 38.07(7) |
| C(17)-C(16)-Ru(2)-C(19) | -80.93(7) |
| C(21)-C(16)-Ru(2)-C(19) | 158.32(13) |
| C(15)-C(16)-Ru(2)-C(18) | 80.78(8) |
| C(17)-C(16)-Ru(2)-C(18) | -38.22(7) |
| C(21)-C(16)-Ru(2)-C(18) | -158.97(13) |

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|---|---|
| C(15)-C(16)-Ru(2)-C(17) | 119.00(10) |
| C(21)-C(16)-Ru(2)-C(17) | -120.75(14) |
| C(17)-C(16)-Ru(2)-C(15) | -119.00(10) |
| C(21)-C(16)-Ru(2)-C(15) | 120.25(14) |
| C(28)-C(27)-N(2)-Ru(2) | 173.18(10) |
| C(25)-Ru(2)-N(2)-C(27) | 70.87(11) |
| C(26)-Ru(2)-N(2)-C(27) | 162.84(11) |
| C(19)-Ru(2)-N(2)-C(27) | -91.87(14) |
| C(18)-Ru(2)-N(2)-C(27) | -24.51(13) |
| C(17)-Ru(2)-N(2)-C(27) | -37.68(11) |
| C(15)-Ru(2)-N(2)-C(27) | -103.37(11) |
| C(16)-Ru(2)-N(2)-C(27) | -74.17(11) |

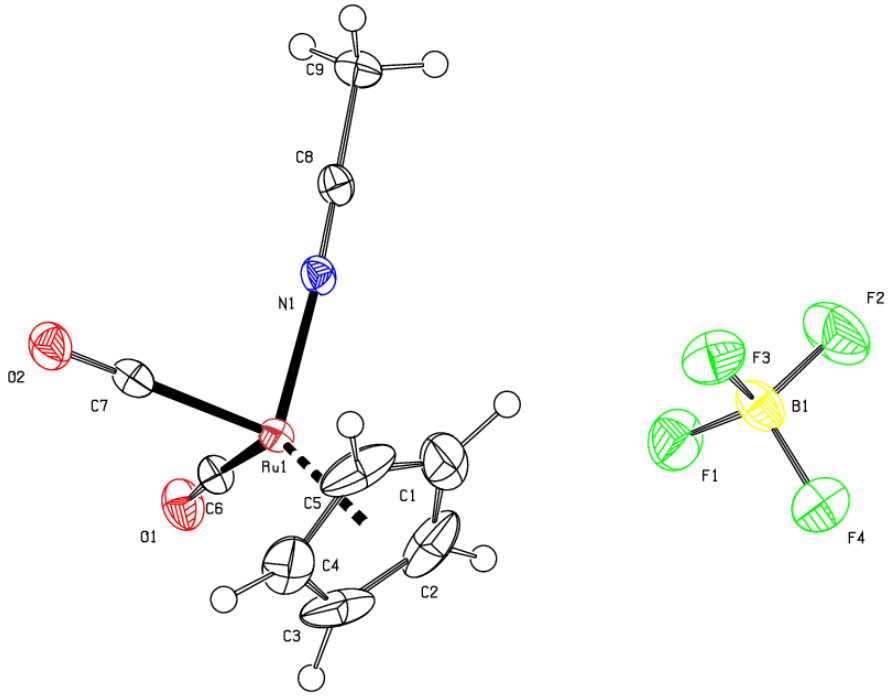
**Table B41:** Hydrogen bonds for $[\eta^5\text{-}C_5(CH_3)_5Ru(CO)_2NH_2CH_2CH_3]BF_4$ [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) | |
|---|---|---|---|---|---|
| N(1)-H(1A)…F(6) | 0.92 | 2.13 | 2.9638(15) | 150 | 1-x,1-y,-z |
| N(1)-H(1B)…F(8) | 0.92 | 2.11 | 3.0196(15) | 170 | -1+x,y,z |
| N(2)-H(2A)…F(3) | 0.92 | 2.24 | 3.1521(15) | 169 | 1+x,y,z |
| N(2)-H(2B)…F(2) | 0.92 | 2.16 | 2.9801(16) | 148 | 1-x,-y,1-z |
| C(21)-H(21A)…F(4) | 0.98 | 2.55 | 3.4191(19) | 148 | 1-x,1-y,1-z |
| C(21)-H(21C)…F(3) | 0.98 | 2.48 | 3.4338(18) | 163 | 1+x,y,z |

For C--H...Acceptor Interactions See: Th. Steiner, Cryst. Rev, (1996), 6, 1-57

# STRUCTURE TABLES PERTAINING TO CHAPTER 5

## Cyclopentadienyl ruthenium(II) acetonitrile complex – $[\eta^5\text{-}C_5H_5Ru(CO)_2NCCH_3]BF_4$




**ORTEP diagrams**

**Table B42:** Crystal data and structure refinement for $[\eta^5\text{-}C_5H_5Ru(CO)_2NCCH_3]BF_4$

| | | |
|---|---|---|
| Empirical formula | C9 H8 B F4 N O2 Ru | |
| Formula weight | 350.04 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P21/c | |
| Unit cell dimensions | a = 6.8540(2) Å | α= 90°. |
| | b = 15.1790(5) Å | β= 94.9170(10)°. |
| | c = 11.5373(4) Å | γ = 90°. |
| Volume | 1195.89(7) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.944 $Mg/m^3$ | |
| Absorption coefficient | 1.353 $mm^{-1}$ | |
| F(000) | 680 | |
| Crystal size | 0.35 x 0.16 x 0.15 $mm^3$ | |
| Theta range for data collection | 2.22 to 27.99°. | |
| Index ranges | -7<=h<=9, -19<=k<=19, -15<=l<=14 | |
| Reflections collected | 18373 | |
| Independent reflections | 2798 [R(int) = 0.0336] | |
| Completeness to theta = 27.99° | 97.5 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.8228 and 0.6488 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2798 / 0 / 164 | |
| Goodness-of-fit on $F^2$ | 1.119 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0264, wR2 = 0.0693 | |
| R indices (all data) | R1 = 0.0290, wR2 = 0.0719 | |
| Largest diff. peak and hole | 1.585 and -0.642 $e.Å^{-3}$ | |

**Table B43:** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $[\eta^5\text{-}C_5H_5Ru(CO)_2NCCH_3]BF_4$. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 5134(6) | 2399(3) | 5106(3) | 52(1) |
| C(2) | 3452(7) | 1974(2) | 5325(3) | 51(1) |
| C(3) | 1970(5) | 2267(3) | 4537(3) | 50(1) |
| C(4) | 2702(6) | 2898(2) | 3812(3) | 47(1) |
| C(5) | 4762(6) | 2980(2) | 4173(3) | 49(1) |
| C(6) | 753(4) | 3382(2) | 6477(2) | 22(1) |
| C(7) | 2488(4) | 4602(2) | 5128(2) | 23(1) |
| C(8) | 5689(4) | 4121(2) | 7768(2) | 21(1) |
| C(9) | 6922(4) | 4491(2) | 8730(2) | 28(1) |
| N(1) | 4735(3) | 3837(1) | 7004(2) | 20(1) |
| O(1) | -598(3) | 3319(1) | 6971(2) | 30(1) |
| O(2) | 2252(3) | 5299(1) | 4798(2) | 32(1) |
| B(1) | 1646(5) | 5648(2) | 8086(3) | 33(1) |
| F(1) | 3497(3) | 5891(1) | 7834(2) | 51(1) |
| F(2) | 413(4) | 5470(2) | 7127(2) | 62(1) |
| F(3) | 841(3) | 6288(1) | 8763(2) | 45(1) |
| F(4) | 1852(3) | 4860(1) | 8734(2) | 45(1) |
| Ru(1) | 2973(1) | 3407(1) | 5585(1) | 17(1) |

**Table B44:** Bond lengths [Å] and angles [°] for $[\eta^5\text{-}C_5H_5Ru(CO)_2NCCH_3]BF_4$.

| | |
|---|---|
| C(1)-C(2) | 1.363(6) |
| C(1)-C(5) | 1.398(6) |
| C(1)-Ru(1) | 2.232(3) |
| C(1)-H(1) | 1.0000 |
| C(2)-C(3) | 1.378(6) |
| C(2)-Ru(1) | 2.223(3) |
| C(2)-H(2) | 1.0000 |
| C(3)-C(4) | 1.393(5) |

| | |
|---|---|
| C(3)-Ru(1) | 2.188(3) |
| C(3)-H(3) | 1.0000 |
| C(4)-C(5) | 1.443(6) |
| C(4)-Ru(1) | 2.179(3) |
| C(4)-H(4) | 1.0000 |
| C(5)-Ru(1) | 2.218(3) |
| C(5)-H(5) | 1.0000 |
| C(6)-O(1) | 1.132(3) |
| C(6)-Ru(1) | 1.909(3) |
| C(7)-O(2) | 1.132(3) |
| C(7)-Ru(1) | 1.910(3) |
| C(8)-N(1) | 1.136(3) |
| C(8)-C(9) | 1.449(4) |
| C(9)-H(9A) | 0.9800 |
| C(9)-H(9B) | 0.9800 |
| C(9)-H(9C) | 0.9800 |
| N(1)-Ru(1) | 2.056(2) |
| B(1)-F(2) | 1.361(4) |
| B(1)-F(1) | 1.376(4) |
| B(1)-F(3) | 1.390(4) |
| B(1)-F(4) | 1.411(4) |

| | |
|---|---|
| C(2)-C(1)-C(5) | 109.9(3) |
| C(2)-C(1)-Ru(1) | 71.8(2) |
| C(5)-C(1)-Ru(1) | 71.15(18) |
| C(2)-C(1)-H(1) | 125.1 |
| C(5)-C(1)-H(1) | 125.1 |
| Ru(1)-C(1)-H(1) | 125.1 |
| C(1)-C(2)-C(3) | 108.2(3) |
| C(1)-C(2)-Ru(1) | 72.5(2) |
| C(3)-C(2)-Ru(1) | 70.4(2) |
| C(1)-C(2)-H(2) | 125.8 |
| C(3)-C(2)-H(2) | 125.8 |
| Ru(1)-C(2)-H(2) | 125.8 |
| C(2)-C(3)-C(4) | 109.5(3) |
| C(2)-C(3)-Ru(1) | 73.21(19) |
| C(4)-C(3)-Ru(1) | 71.05(18) |
| C(2)-C(3)-H(3) | 125.2 |

| | |
|---|---|
| C(4)-C(3)-H(3) | 125.2 |
| Ru(1)-C(3)-H(3) | 125.2 |
| C(3)-C(4)-C(5) | 106.3(3) |
| C(3)-C(4)-Ru(1) | 71.74(18) |
| C(5)-C(4)-Ru(1) | 72.31(17) |
| C(3)-C(4)-H(4) | 126.7 |
| C(5)-C(4)-H(4) | 126.7 |
| Ru(1)-C(4)-H(4) | 126.7 |
| C(1)-C(5)-C(4) | 106.1(3) |
| C(1)-C(5)-Ru(1) | 72.23(18) |
| C(4)-C(5)-Ru(1) | 69.39(17) |
| C(1)-C(5)-H(5) | 126.9 |
| C(4)-C(5)-H(5) | 126.9 |
| Ru(1)-C(5)-H(5) | 126.9 |
| O(1)-C(6)-Ru(1) | 175.6(2) |
| O(2)-C(7)-Ru(1) | 175.9(2) |
| N(1)-C(8)-C(9) | 179.1(3) |
| C(8)-C(9)-H(9A) | 109.5 |
| C(8)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 109.5 |
| C(8)-C(9)-H(9C) | 109.5 |
| H(9A)-C(9)-H(9C) | 109.5 |
| H(9B)-C(9)-H(9C) | 109.5 |
| C(8)-N(1)-Ru(1) | 176.2(2) |
| F(2)-B(1)-F(1) | 113.6(3) |
| F(2)-B(1)-F(3) | 110.3(3) |
| F(1)-B(1)-F(3) | 110.4(3) |
| F(2)-B(1)-F(4) | 106.9(3) |
| F(1)-B(1)-F(4) | 106.7(3) |
| F(3)-B(1)-F(4) | 108.7(3) |
| C(6)-Ru(1)-C(7) | 92.26(10) |
| C(6)-Ru(1)-N(1) | 91.01(10) |
| C(7)-Ru(1)-N(1) | 89.68(10) |
| C(6)-Ru(1)-C(4) | 119.46(14) |
| C(7)-Ru(1)-C(4) | 94.53(12) |
| N(1)-Ru(1)-C(4) | 148.96(13) |
| C(6)-Ru(1)-C(3) | 93.19(11) |
| C(7)-Ru(1)-C(3) | 124.05(14) |

| | |
|---|---|
| N(1)-Ru(1)-C(3) | 145.74(13) |
| C(4)-Ru(1)-C(3) | 37.21(14) |
| C(6)-Ru(1)-C(5) | 155.08(12) |
| C(7)-Ru(1)-C(5) | 99.73(13) |
| N(1)-Ru(1)-C(5) | 110.68(12) |
| C(4)-Ru(1)-C(5) | 38.30(15) |
| C(3)-Ru(1)-C(5) | 62.00(12) |
| C(6)-Ru(1)-C(2) | 100.81(13) |
| C(7)-Ru(1)-C(2) | 156.34(12) |
| N(1)-Ru(1)-C(2) | 109.53(13) |
| C(4)-Ru(1)-C(2) | 61.87(13) |
| C(3)-Ru(1)-C(2) | 36.39(16) |
| C(5)-Ru(1)-C(2) | 61.18(13) |
| C(6)-Ru(1)-C(1) | 134.16(14) |
| C(7)-Ru(1)-C(1) | 133.33(15) |
| N(1)-Ru(1)-C(1) | 93.29(11) |
| C(4)-Ru(1)-C(1) | 61.95(13) |
| C(3)-Ru(1)-C(1) | 60.32(14) |
| C(5)-Ru(1)-C(1) | 36.62(15) |
| C(2)-Ru(1)-C(1) | 35.64(16) |

---

Symmetry transformations used to generate equivalent atoms:

**Table B45:** Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $[\eta^5\text{-}C_5H_5Ru(CO)_2NCCH_3]BF_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 49(2) | 58(2) | 47(2) | -29(2) | -11(2) | 28(2) |
| C(2) | 97(3) | 24(2) | 35(2) | -4(1) | 18(2) | 8(2) |
| C(3) | 46(2) | 49(2) | 57(2) | -35(2) | 20(2) | -23(2) |
| C(4) | 74(3) | 44(2) | 21(2) | -12(1) | -9(2) | 17(2) |
| C(5) | 61(2) | 37(2) | 56(2) | -27(2) | 42(2) | -22(2) |
| C(6) | 21(1) | 22(1) | 23(1) | 1(1) | -2(1) | 2(1) |
| C(7) | 18(1) | 29(1) | 21(1) | 2(1) | -1(1) | -2(1) |
| C(8) | 18(1) | 24(1) | 21(1) | 1(1) | 3(1) | 3(1) |
| C(9) | 26(1) | 31(1) | 24(1) | -3(1) | -3(1) | -4(1) |
| N(1) | 17(1) | 23(1) | 22(1) | -1(1) | 2(1) | 3(1) |
| O(1) | 22(1) | 34(1) | 35(1) | 7(1) | 7(1) | 3(1) |
| O(2) | 29(1) | 29(1) | 37(1) | 10(1) | -2(1) | -1(1) |
| B(1) | 27(2) | 43(2) | 28(2) | -10(1) | 1(1) | 1(1) |
| F(1) | 35(1) | 45(1) | 77(2) | 2(1) | 16(1) | -2(1) |
| F(2) | 61(1) | 80(2) | 42(1) | -10(1) | -19(1) | 0(1) |
| F(3) | 52(1) | 39(1) | 44(1) | -6(1) | 12(1) | 14(1) |
| F(4) | 50(1) | 39(1) | 48(1) | 4(1) | 7(1) | 3(1) |
| Ru(1) | 17(1) | 19(1) | 16(1) | 0(1) | 0(1) | 0(1) |

**Table B46:** Hydrogen coordinates ( x 104) and isotropic displacement parameters ($Å^2$x $10^3$) for [$\eta^5$-$C_5H_5Ru(CO)_2NCCH_3$]$BF_4$.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 6447 | 2295 | 5532 | 63 |
| H(2) | 3333 | 1503 | 5921 | 62 |
| H(3) | 601 | 2033 | 4462 | 60 |
| H(4) | 1984 | 3180 | 3118 | 56 |
| H(5) | 5746 | 3341 | 3791 | 59 |
| H(9A) | 7941 | 4857 | 8427 | 41 |
| H(9B) | 7535 | 4013 | 9203 | 41 |
| H(9C) | 6124 | 4853 | 9211 | 41 |

**Table B47:** Torsion angles [°] for [$\eta^5$-$C_5H_5Ru(CO)_2NCCH_3$]$BF_4$.

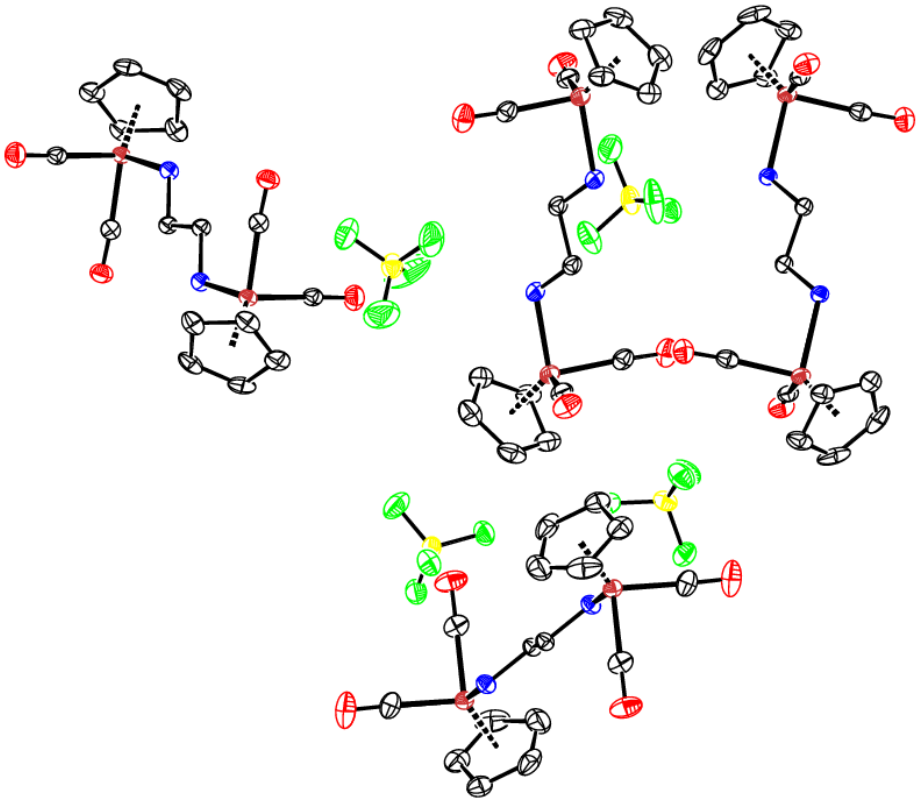
| | |
|---|---|
| C(5)-C(1)-C(2)-C(3) | 0.4(4) |
| Ru(1)-C(1)-C(2)-C(3) | 61.7(2) |
| C(5)-C(1)-C(2)-Ru(1) | -61.3(2) |
| C(1)-C(2)-C(3)-C(4) | -0.9(4) |
| Ru(1)-C(2)-C(3)-C(4) | 62.2(2) |
| C(1)-C(2)-C(3)-Ru(1) | -63.1(2) |
| C(2)-C(3)-C(4)-C(5) | 1.0(4) |
| Ru(1)-C(3)-C(4)-C(5) | 64.6(2) |
| C(2)-C(3)-C(4)-Ru(1) | -63.5(2) |
| C(2)-C(1)-C(5)-C(4) | 0.2(4) |
| Ru(1)-C(1)-C(5)-C(4) | -61.5(2) |
| C(2)-C(1)-C(5)-Ru(1) | 61.7(2) |
| C(3)-C(4)-C(5)-C(1) | -0.8(3) |
| Ru(1)-C(4)-C(5)-C(1) | 63.4(2) |
| C(3)-C(4)-C(5)-Ru(1) | -64.2(2) |
| C(9)-C(8)-N(1)-Ru(1) | -52(20) |

| | |
|---|---|
| O(1)-C(6)-Ru(1)-C(7) | 130(3) |
| O(1)-C(6)-Ru(1)-N(1) | -140(3) |
| O(1)-C(6)-Ru(1)-C(4) | 34(3) |
| O(1)-C(6)-Ru(1)-C(3) | 6(3) |
| O(1)-C(6)-Ru(1)-C(5) | 11(3) |
| O(1)-C(6)-Ru(1)-C(2) | -30(3) |
| O(1)-C(6)-Ru(1)-C(1) | -45(3) |
| O(2)-C(7)-Ru(1)-C(6) | -151(3) |
| O(2)-C(7)-Ru(1)-N(1) | 118(3) |
| O(2)-C(7)-Ru(1)-C(4) | -31(3) |
| O(2)-C(7)-Ru(1)-C(3) | -55(3) |
| O(2)-C(7)-Ru(1)-C(5) | 7(3) |
| O(2)-C(7)-Ru(1)-C(2) | -27(3) |
| O(2)-C(7)-Ru(1)-C(1) | 24(3) |
| C(8)-N(1)-Ru(1)-C(6) | -93(3) |
| C(8)-N(1)-Ru(1)-C(7) | 0(3) |
| C(8)-N(1)-Ru(1)-C(4) | 98(3) |
| C(8)-N(1)-Ru(1)-C(3) | 170(3) |
| C(8)-N(1)-Ru(1)-C(5) | 100(3) |
| C(8)-N(1)-Ru(1)-C(2) | 166(3) |
| C(8)-N(1)-Ru(1)-C(1) | 133(3) |
| C(3)-C(4)-Ru(1)-C(6) | -50.3(3) |
| C(5)-C(4)-Ru(1)-C(6) | -164.85(19) |
| C(3)-C(4)-Ru(1)-C(7) | -145.5(2) |
| C(5)-C(4)-Ru(1)-C(7) | 100.0(2) |
| C(3)-C(4)-Ru(1)-N(1) | 117.5(3) |
| C(5)-C(4)-Ru(1)-N(1) | 3.0(3) |
| C(5)-C(4)-Ru(1)-C(3) | -114.5(3) |
| C(3)-C(4)-Ru(1)-C(5) | 114.5(3) |
| C(3)-C(4)-Ru(1)-C(2) | 36.3(2) |
| C(5)-C(4)-Ru(1)-C(2) | -78.2(2) |
| C(3)-C(4)-Ru(1)-C(1) | 76.9(3) |
| C(5)-C(4)-Ru(1)-C(1) | -37.6(2) |
| C(2)-C(3)-Ru(1)-C(6) | -103.9(2) |
| C(4)-C(3)-Ru(1)-C(6) | 137.8(2) |
| C(2)-C(3)-Ru(1)-C(7) | 161.2(2) |
| C(4)-C(3)-Ru(1)-C(7) | 42.9(3) |
| C(2)-C(3)-Ru(1)-N(1) | -7.4(3) |

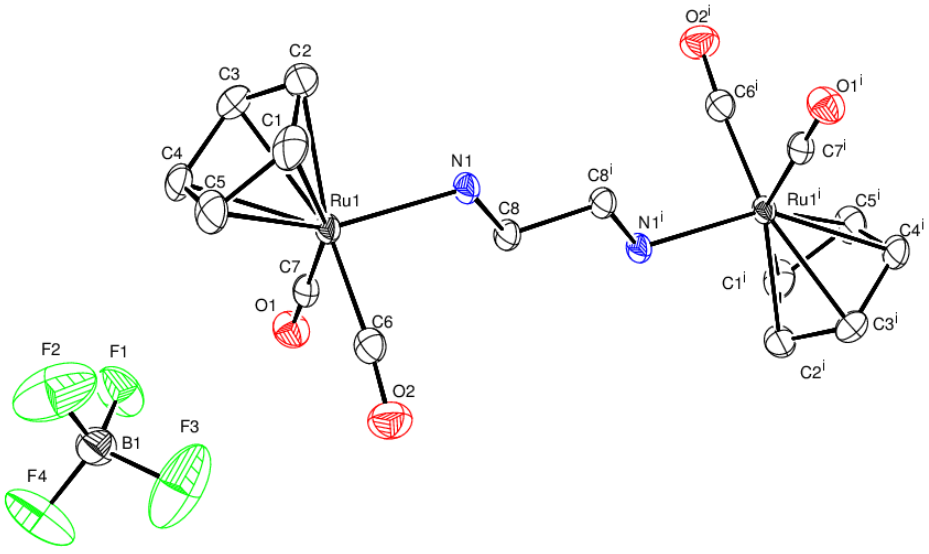
| | |
|---|---|
| C(4)-C(3)-Ru(1)-N(1) | -125.7(3) |
| C(2)-C(3)-Ru(1)-C(4) | 118.2(3) |
| C(2)-C(3)-Ru(1)-C(5) | 78.5(3) |
| C(4)-C(3)-Ru(1)-C(5) | -39.7(2) |
| C(4)-C(3)-Ru(1)-C(2) | -118.2(3) |
| C(2)-C(3)-Ru(1)-C(1) | 36.5(2) |
| C(4)-C(3)-Ru(1)-C(1) | -81.7(2) |
| C(1)-C(5)-Ru(1)-C(6) | -82.9(4) |
| C(4)-C(5)-Ru(1)-C(6) | 32.7(4) |
| C(1)-C(5)-Ru(1)-C(7) | 159.5(2) |
| C(4)-C(5)-Ru(1)-C(7) | -85.0(2) |
| C(1)-C(5)-Ru(1)-N(1) | 66.1(2) |
| C(4)-C(5)-Ru(1)-N(1) | -178.34(19) |
| C(1)-C(5)-Ru(1)-C(4) | -115.6(3) |
| C(1)-C(5)-Ru(1)-C(3) | -77.0(2) |
| C(4)-C(5)-Ru(1)-C(3) | 38.5(2) |
| C(1)-C(5)-Ru(1)-C(2) | -35.4(2) |
| C(4)-C(5)-Ru(1)-C(2) | 80.1(2) |
| C(4)-C(5)-Ru(1)-C(1) | 115.6(3) |
| C(1)-C(2)-Ru(1)-C(6) | -162.0(2) |
| C(3)-C(2)-Ru(1)-C(6) | 80.6(2) |
| C(1)-C(2)-Ru(1)-C(7) | 75.6(4) |
| C(3)-C(2)-Ru(1)-C(7) | -41.8(5) |
| C(1)-C(2)-Ru(1)-N(1) | -67.0(2) |
| C(3)-C(2)-Ru(1)-N(1) | 175.6(2) |
| C(1)-C(2)-Ru(1)-C(4) | 80.2(2) |
| C(3)-C(2)-Ru(1)-C(4) | -37.2(2) |
| C(1)-C(2)-Ru(1)-C(3) | 117.4(3) |
| C(1)-C(2)-Ru(1)-C(5) | 36.4(2) |
| C(3)-C(2)-Ru(1)-C(5) | -81.0(2) |
| C(3)-C(2)-Ru(1)-C(1) | -117.4(3) |
| C(2)-C(1)-Ru(1)-C(6) | 25.0(3) |
| C(5)-C(1)-Ru(1)-C(6) | 144.3(2) |
| C(2)-C(1)-Ru(1)-C(7) | -147.7(2) |
| C(5)-C(1)-Ru(1)-C(7) | -28.4(3) |
| C(2)-C(1)-Ru(1)-N(1) | 119.6(2) |
| C(5)-C(1)-Ru(1)-N(1) | -121.0(2) |
| C(2)-C(1)-Ru(1)-C(4) | -80.0(2) |

| | |
|---|---|
| C(5)-C(1)-Ru(1)-C(4) | 39.3(2) |
| C(2)-C(1)-Ru(1)-C(3) | -37.3(2) |
| C(5)-C(1)-Ru(1)-C(3) | 82.0(2) |
| C(2)-C(1)-Ru(1)-C(5) | -119.3(3) |
| C(5)-C(1)-Ru(1)-C(2) | 119.3(3) |

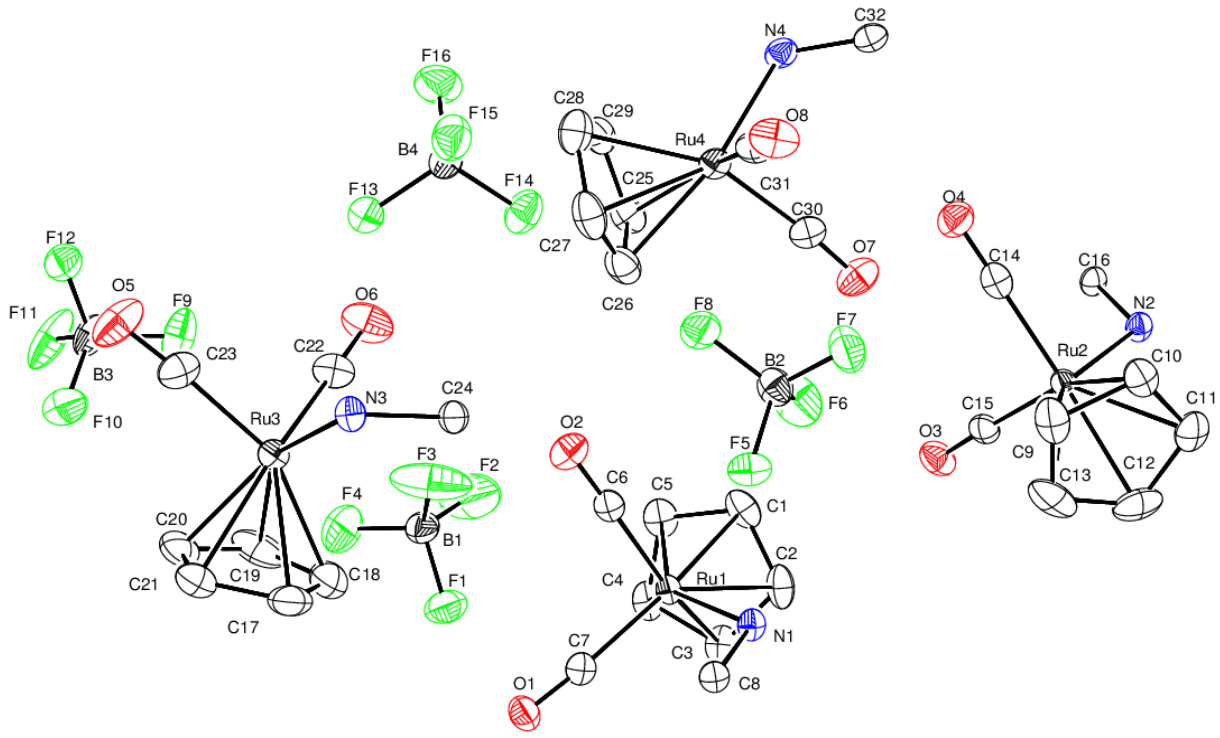
## Cyclopentadienyl ruthenium(II) 1,2-diethylamine complex – $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$ (Polymorph 1)



**Four grown cations and four anions**




(b) **One grown cation and one anion**




**(c) Four half molecules of the cation and four molecules of the anion**

**ORTEP diagram**

**Table B47:** Crystal data and structure refinement for $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$.

| | | |
|---|---|---|
| Formula weight | 678.08 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 11.7324(3) Å | α= 92.8290(10)°. |
| | b = 13.9727(3) Å | β= 93.3210(10)°. |
| | c = 14.1296(3) Å | γ = 98.9230(10)°. |
| Volume | 2280.44(9) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.975 $Mg/m^3$ | |
| Absorption coefficient | 1.415 $mm^{-1}$ | |

| | |
|---|---|
| F(000) | 1320 |
| Crystal size | 0.45 x 0.33 x 0.26 $mm^3$ |
| Theta range for data collection | 1.45 to 28.00°. |
| Index ranges | -15<=h<=15, -18<=k<=18, -18<=l<=18 |
| Reflections collected | 53134 |
| Independent reflections | 10821 [R(int) = 0.0213] |
| Completeness to theta = 28.00° | 98.2 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7098 and 0.5684 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 10821 / 0 / 613 |
| Goodness-of-fit on $F^2$ | 1.048 |
| Final R indices [I>2sigma(I)] | R1 = 0.0357, wR2 = 0.0873 |
| R indices (all data) | R1 = 0.0465, wR2 = 0.0938 |
| Largest diff. peak and hole | 2.155 and -1.092 e.$Å^{-3}$ |

**Table B48:** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $\{\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 9800(4) | 5015(3) | 3818(3) | 31(1) |
| C(2) | 10907(4) | 5220(3) | 3480(3) | 31(1) |
| C(3) | 11260(4) | 6248(3) | 3507(3) | 30(1) |
| C(4) | 10340(4) | 6679(3) | 3893(3) | 28(1) |
| C(5) | 9447(4) | 5921(3) | 4087(3) | 31(1) |
| C(6) | 8047(3) | 5588(3) | 2252(2) | 23(1) |
| C(7) | 9671(3) | 7015(3) | 1849(2) | 22(1) |
| C(8) | 9885(3) | 5367(3) | 382(2) | 20(1) |
| C(9) | 9369(4) | 901(3) | 954(3) | 33(1) |
| C(10) | 9548(4) | -63(3) | 1149(3) | 28(1) |
| C(11) | 10708(4) | -15(3) | 1485(3) | 30(1) |
| C(12) | 11254(4) | 962(4) | 1514(3) | 40(1) |
| C(13) | 10419(5) | 1523(3) | 1176(3) | 42(1) |
| C(14) | 8229(3) | 750(3) | 2762(3) | 25(1) |
| C(15) | 10196(3) | 2092(3) | 3214(3) | 24(1) |
| C(16) | 9810(3) | 328(3) | 4627(2) | 20(1) |
| C(17) | 6057(4) | 8112(3) | 161(4) | 43(1) |
| C(18) | 6484(4) | 8076(4) | 1105(4) | 51(1) |
| C(19) | 5878(5) | 8671(3) | 1679(4) | 47(1) |
| C(20) | 5090(4) | 9048(3) | 1086(3) | 37(1) |
| C(21) | 5190(4) | 8700(3) | 143(3) | 33(1) |
| C(22) | 4470(4) | 6762(3) | 2124(3) | 31(1) |
| C(23) | 3007(4) | 7531(3) | 960(3) | 32(1) |
| C(24) | 5126(3) | 5437(3) | 352(2) | 21(1) |
| C(25) | 5744(4) | 3974(3) | 4997(3) | 32(1) |
| C(26) | 5957(4) | 4130(3) | 4022(3) | 37(1) |
| C(27) | 4914(4) | 3847(3) | 3474(3) | 39(1) |
| C(28) | 4037(4) | 3492(3) | 4091(3) | 38(1) |
| C(29) | 4567(4) | 3588(3) | 5031(3) | 31(1) |
| C(30) | 6979(3) | 2340(3) | 4273(3) | 27(1) |
| C(31) | 5077(3) | 1798(3) | 2963(3) | 29(1) |
| C(32) | 5213(3) | 388(3) | 4662(3) | 24(1) |
| B(1) | 7707(4) | 8048(4) | 3859(4) | 33(1) |

| | | | | |
|---|---|---|---|---|
| B(2) | 7437(4) | 3048(4) | 1564(3) | 31(1) |
| B(3) | 2697(4) | 9016(4) | 3213(3) | 33(1) |
| B(4) | 2578(4) | 3898(3) | 1261(3) | 30(1) |
| N(1) | 10030(3) | 5012(2) | 1342(2) | 20(1) |
| N(2) | 10245(3) | 99(2) | 3689(2) | 20(1) |
| N(3) | 4338(3) | 6144(2) | 142(2) | 22(1) |
| N(4) | 4850(3) | 1328(2) | 4927(2) | 26(1) |
| O(1) | 9628(2) | 7701(2) | 1460(2) | 30(1) |
| O(2) | 7054(2) | 5443(2) | 2133(2) | 35(1) |
| O(3) | 10443(3) | 2829(2) | 3605(2) | 33(1) |
| O(4) | 7257(2) | 654(2) | 2853(2) | 33(1) |
| O(5) | 2069(3) | 7635(3) | 945(3) | 49(1) |
| O(6) | 4384(3) | 6361(3) | 2808(2) | 45(1) |
| O(7) | 7939(3) | 2286(2) | 4379(2) | 38(1) |
| O(8) | 4843(3) | 1394(2) | 2250(2) | 39(1) |
| F(1) | 8667(2) | 8316(2) | 3352(2) | 49(1) |
| F(2) | 8015(3) | 7685(4) | 4673(3) | 88(1) |
| F(3) | 6959(4) | 7347(3) | 3321(3) | 89(1) |
| F(4) | 7184(3) | 8835(3) | 3974(3) | 79(1) |
| F(5) | 7906(2) | 3657(2) | 872(2) | 35(1) |
| F(6) | 8137(3) | 3220(2) | 2397(2) | 53(1) |
| F(7) | 7324(2) | 2091(2) | 1237(2) | 43(1) |
| F(8) | 6340(2) | 3272(2) | 1723(2) | 37(1) |
| F(9) | 3428(3) | 8381(2) | 3500(2) | 51(1) |
| F(10) | 3110(2) | 9472(2) | 2427(2) | 50(1) |
| F(11) | 2661(2) | 9735(3) | 3929(2) | 61(1) |
| F(12) | 1591(2) | 8526(2) | 2995(2) | 37(1) |
| F(13) | 2602(2) | 4898(2) | 1164(2) | 38(1) |
| F(14) | 3700(2) | 3711(2) | 1428(2) | 37(1) |
| F(15) | 2104(2) | 3402(2) | 426(2) | 39(1) |
| F(16) | 1908(3) | 3624(2) | 2005(2) | 48(1) |
| Ru(1) | 9652(1) | 5880(1) | 2546(1) | 17(1) |
| Ru(2) | 9811(1) | 891(1) | 2487(1) | 20(1) |
| Ru(3) | 4616(1) | 7464(1) | 1020(1) | 21(1) |
| Ru(4) | 5424(1) | 2562(1) | 4130(1) | 23(1) |

**Table B49:** Bond lengths [Å] and angles [°] for $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$.

| | |
|---|---|
| C(1)-C(2) | 1.402(6) |
| C(1)-C(5) | 1.433(6) |
| C(1)-Ru(1) | 2.228(4) |
| C(1)-H(1) | 1.0000 |
| C(2)-C(3) | 1.430(6) |
| C(2)-Ru(1) | 2.253(4) |
| C(2)-H(2) | 1.0000 |
| C(3)-C(4) | 1.435(6) |
| C(3)-Ru(1) | 2.236(4) |
| C(3)-H(3) | 1.0000 |
| C(4)-C(5) | 1.418(6) |
| C(4)-Ru(1) | 2.203(4) |
| C(4)-H(4) | 1.0000 |
| C(5)-Ru(1) | 2.202(4) |
| C(5)-H(5) | 1.0000 |
| C(6)-O(2) | 1.152(5) |
| C(6)-Ru(1) | 1.882(4) |
| C(7)-O(1) | 1.135(4) |
| C(7)-Ru(1) | 1.906(4) |
| C(8)-N(1) | 1.477(4) |
| C(8)-C(8)#1 | 1.516(6) |
| C(8)-H(8A) | 0.9900 |
| C(8)-H(8B) | 0.9900 |
| C(9)-C(13) | 1.402(7) |
| C(9)-C(10) | 1.432(6) |
| C(9)-Ru(2) | 2.199(4) |
| C(9)-H(9) | 1.0000 |
| C(10)-C(11) | 1.405(6) |
| C(10)-Ru(2) | 2.236(4) |
| C(10)-H(10) | 1.0000 |
| C(11)-C(12) | 1.412(6) |
| C(11)-Ru(2) | 2.263(4) |
| C(11)-H(11) | 1.0000 |
| C(12)-C(13) | 1.422(7) |
| C(12)-Ru(2) | 2.235(4) |
| C(12)-H(12) | 1.0000 |

| | |
|---|---|
| C(13)-Ru(2) | 2.199(4) |
| C(13)-H(13) | 1.0000 |
| C(14)-O(4) | 1.143(5) |
| C(14)-Ru(2) | 1.901(4) |
| C(15)-O(3) | 1.133(5) |
| C(15)-Ru(2) | 1.901(4) |
| C(16)-N(2) | 1.486(4) |
| C(16)-C(16)#2 | 1.522(7) |
| C(16)-H(16A) | 0.9900 |
| C(16)-H(16B) | 0.9900 |
| C(17)-C(21) | 1.402(6) |
| C(17)-C(18) | 1.404(8) |
| C(17)-Ru(3) | 2.241(4) |
| C(17)-H(17) | 1.0000 |
| C(18)-C(19) | 1.427(8) |
| C(18)-Ru(3) | 2.220(5) |
| C(18)-H(18) | 1.0000 |
| C(19)-C(20) | 1.392(7) |
| C(19)-Ru(3) | 2.195(4) |
| C(19)-H(19) | 1.0000 |
| C(20)-C(21) | 1.414(6) |
| C(20)-Ru(3) | 2.193(4) |
| C(20)-H(20) | 1.0000 |
| C(21)-Ru(3) | 2.218(4) |
| C(21)-H(21) | 1.0000 |
| C(22)-O(6) | 1.142(5) |
| C(22)-Ru(3) | 1.886(4) |
| C(23)-O(5) | 1.132(5) |
| C(23)-Ru(3) | 1.901(4) |
| C(24)-N(3) | 1.482(4) |
| C(24)-C(24)#3 | 1.518(7) |
| C(24)-H(24A) | 0.9900 |
| C(24)-H(24B) | 0.9900 |
| C(25)-C(29) | 1.407(6) |
| C(25)-C(26) | 1.435(6) |
| C(25)-Ru(4) | 2.240(4) |
| C(25)-H(25) | 1.0000 |
| C(26)-C(27) | 1.401(7) |

| | |
|---|---|
| C(26)-Ru(4) | 2.199(4) |
| C(26)-H(26) | 1.0000 |
| C(27)-C(28) | 1.433(7) |
| C(27)-Ru(4) | 2.207(4) |
| C(27)-H(27) | 1.0000 |
| C(28)-C(29) | 1.425(6) |
| C(28)-Ru(4) | 2.234(4) |
| C(28)-H(28) | 1.0000 |
| C(29)-Ru(4) | 2.259(4) |
| C(29)-H(29) | 1.0000 |
| C(30)-O(7) | 1.142(5) |
| C(30)-Ru(4) | 1.899(4) |
| C(31)-O(8) | 1.128(5) |
| C(31)-Ru(4) | 1.906(4) |
| C(32)-N(4) | 1.480(5) |
| C(32)-C(32)#4 | 1.527(7) |
| C(32)-H(32A) | 0.9900 |
| C(32)-H(32B) | 0.9900 |
| B(1)-F(2) | 1.333(6) |
| B(1)-F(4) | 1.347(6) |
| B(1)-F(3) | 1.374(6) |
| B(1)-F(1) | 1.382(5) |
| B(2)-F(7) | 1.378(6) |
| B(2)-F(6) | 1.384(5) |
| B(2)-F(8) | 1.399(5) |
| B(2)-F(5) | 1.408(5) |
| B(3)-F(12) | 1.381(5) |
| B(3)-F(10) | 1.383(6) |
| B(3)-F(9) | 1.385(5) |
| B(3)-F(11) | 1.397(5) |
| B(4)-F(15) | 1.380(6) |
| B(4)-F(16) | 1.381(5) |
| B(4)-F(14) | 1.391(5) |
| B(4)-F(13) | 1.407(5) |
| N(1)-Ru(1) | 2.147(3) |
| N(1)-H(1A) | 0.9200 |
| N(1)-H(1B) | 0.9200 |
| N(2)-Ru(2) | 2.151(3) |

| | |
|---|---|
| N(2)-H(2A) | 0.9200 |
| N(2)-H(2B) | 0.9200 |
| N(3)-Ru(3) | 2.142(3) |
| N(3)-H(3A) | 0.9200 |
| N(3)-H(3B) | 0.9200 |
| N(4)-Ru(4) | 2.148(3) |
| N(4)-H(4A) | 0.9200 |
| N(4)-H(4B) | 0.9200 |

| | |
|---|---|
| C(2)-C(1)-C(5) | 107.7(4) |
| C(2)-C(1)-Ru(1) | 72.7(2) |
| C(5)-C(1)-Ru(1) | 70.2(2) |
| C(2)-C(1)-H(1) | 126.1 |
| C(5)-C(1)-H(1) | 126.1 |
| Ru(1)-C(1)-H(1) | 126.1 |
| C(1)-C(2)-C(3) | 109.3(4) |
| C(1)-C(2)-Ru(1) | 70.8(2) |
| C(3)-C(2)-Ru(1) | 70.8(2) |
| C(1)-C(2)-H(2) | 125.3 |
| C(3)-C(2)-H(2) | 125.3 |
| Ru(1)-C(2)-H(2) | 125.3 |
| C(2)-C(3)-C(4) | 106.7(4) |
| C(2)-C(3)-Ru(1) | 72.1(2) |
| C(4)-C(3)-Ru(1) | 69.9(2) |
| C(2)-C(3)-H(3) | 126.6 |
| C(4)-C(3)-H(3) | 126.6 |
| Ru(1)-C(3)-H(3) | 126.6 |
| C(5)-C(4)-C(3) | 108.2(4) |
| C(5)-C(4)-Ru(1) | 71.2(2) |
| C(3)-C(4)-Ru(1) | 72.4(2) |
| C(5)-C(4)-H(4) | 125.8 |
| C(3)-C(4)-H(4) | 125.8 |
| Ru(1)-C(4)-H(4) | 125.8 |
| C(4)-C(5)-C(1) | 108.1(4) |
| C(4)-C(5)-Ru(1) | 71.2(2) |
| C(1)-C(5)-Ru(1) | 72.1(2) |
| C(4)-C(5)-H(5) | 125.9 |
| C(1)-C(5)-H(5) | 125.9 |

| | |
|---|---|
| Ru(1)-C(5)-H(5) | 125.9 |
| O(2)-C(6)-Ru(1) | 175.2(3) |
| O(1)-C(7)-Ru(1) | 176.0(3) |
| N(1)-C(8)-C(8)#1 | 111.8(4) |
| N(1)-C(8)-H(8A) | 109.3 |
| C(8)#1-C(8)-H(8A) | 109.3 |
| N(1)-C(8)-H(8B) | 109.3 |
| C(8)#1-C(8)-H(8B) | 109.3 |
| H(8A)-C(8)-H(8B) | 107.9 |
| C(13)-C(9)-C(10) | 107.7(4) |
| C(13)-C(9)-Ru(2) | 71.4(2) |
| C(10)-C(9)-Ru(2) | 72.5(2) |
| C(13)-C(9)-H(9) | 126.0 |
| C(10)-C(9)-H(9) | 126.0 |
| Ru(2)-C(9)-H(9) | 126.0 |
| C(11)-C(10)-C(9) | 107.7(4) |
| C(11)-C(10)-Ru(2) | 72.8(2) |
| C(9)-C(10)-Ru(2) | 69.8(2) |
| C(11)-C(10)-H(10) | 126.1 |
| C(9)-C(10)-H(10) | 126.1 |
| Ru(2)-C(10)-H(10) | 126.1 |
| C(10)-C(11)-C(12) | 108.7(4) |
| C(10)-C(11)-Ru(2) | 70.8(2) |
| C(12)-C(11)-Ru(2) | 70.6(2) |
| C(10)-C(11)-H(11) | 125.7 |
| C(12)-C(11)-H(11) | 125.7 |
| Ru(2)-C(11)-H(11) | 125.7 |
| C(11)-C(12)-C(13) | 107.4(4) |
| C(11)-C(12)-Ru(2) | 72.8(2) |
| C(13)-C(12)-Ru(2) | 69.9(2) |
| C(11)-C(12)-H(12) | 126.2 |
| C(13)-C(12)-H(12) | 126.2 |
| Ru(2)-C(12)-H(12) | 126.2 |
| C(9)-C(13)-C(12) | 108.6(4) |
| C(9)-C(13)-Ru(2) | 71.4(2) |
| C(12)-C(13)-Ru(2) | 72.7(2) |
| C(9)-C(13)-H(13) | 125.6 |
| C(12)-C(13)-H(13) | 125.6 |

| | |
|---|---|
| Ru(2)-C(13)-H(13) | 125.6 |
| O(4)-C(14)-Ru(2) | 174.6(3) |
| O(3)-C(15)-Ru(2) | 176.4(3) |
| N(2)-C(16)-C(16)#2 | 111.3(3) |
| N(2)-C(16)-H(16A) | 109.4 |
| C(16)#2-C(16)-H(16A) | 109.4 |
| N(2)-C(16)-H(16B) | 109.4 |
| C(16)#2-C(16)-H(16B) | 109.4 |
| H(16A)-C(16)-H(16B) | 108.0 |
| C(21)-C(17)-C(18) | 108.7(4) |
| C(21)-C(17)-Ru(3) | 70.8(2) |
| C(18)-C(17)-Ru(3) | 70.8(3) |
| C(21)-C(17)-H(17) | 125.6 |
| C(18)-C(17)-H(17) | 125.6 |
| Ru(3)-C(17)-H(17) | 125.6 |
| C(17)-C(18)-C(19) | 107.1(4) |
| C(17)-C(18)-Ru(3) | 72.5(3) |
| C(19)-C(18)-Ru(3) | 70.2(3) |
| C(17)-C(18)-H(18) | 126.3 |
| C(19)-C(18)-H(18) | 126.3 |
| Ru(3)-C(18)-H(18) | 126.3 |
| C(20)-C(19)-C(18) | 108.1(4) |
| C(20)-C(19)-Ru(3) | 71.4(3) |
| C(18)-C(19)-Ru(3) | 72.1(3) |
| C(20)-C(19)-H(19) | 125.9 |
| C(18)-C(19)-H(19) | 125.9 |
| Ru(3)-C(19)-H(19) | 125.9 |
| C(19)-C(20)-C(21) | 108.4(4) |
| C(19)-C(20)-Ru(3) | 71.6(3) |
| C(21)-C(20)-Ru(3) | 72.3(2) |
| C(19)-C(20)-H(20) | 125.7 |
| C(21)-C(20)-H(20) | 125.7 |
| Ru(3)-C(20)-H(20) | 125.7 |
| C(17)-C(21)-C(20) | 107.7(4) |
| C(17)-C(21)-Ru(3) | 72.6(2) |
| C(20)-C(21)-Ru(3) | 70.3(2) |
| C(17)-C(21)-H(21) | 126.1 |
| C(20)-C(21)-H(21) | 126.1 |

| | |
|---|---|
| Ru(3)-C(21)-H(21) | 126.1 |
| O(6)-C(22)-Ru(3) | 178.1(4) |
| O(5)-C(23)-Ru(3) | 175.4(4) |
| N(3)-C(24)-C(24)#3 | 110.7(3) |
| N(3)-C(24)-H(24A) | 109.5 |
| C(24)#3-C(24)-H(24A) | 109.5 |
| N(3)-C(24)-H(24B) | 109.5 |
| C(24)#3-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 108.1 |
| C(29)-C(25)-C(26) | 107.6(4) |
| C(29)-C(25)-Ru(4) | 72.5(2) |
| C(26)-C(25)-Ru(4) | 69.6(2) |
| C(29)-C(25)-H(25) | 126.2 |
| C(26)-C(25)-H(25) | 126.2 |
| Ru(4)-C(25)-H(25) | 126.2 |
| C(27)-C(26)-C(25) | 108.2(4) |
| C(27)-C(26)-Ru(4) | 71.8(3) |
| C(25)-C(26)-Ru(4) | 72.7(2) |
| C(27)-C(26)-H(26) | 125.8 |
| C(25)-C(26)-H(26) | 125.8 |
| Ru(4)-C(26)-H(26) | 125.8 |
| C(26)-C(27)-C(28) | 108.5(4) |
| C(26)-C(27)-Ru(4) | 71.1(2) |
| C(28)-C(27)-Ru(4) | 72.2(2) |
| C(26)-C(27)-H(27) | 125.7 |
| C(28)-C(27)-H(27) | 125.7 |
| Ru(4)-C(27)-H(27) | 125.7 |
| C(29)-C(28)-C(27) | 107.0(4) |
| C(29)-C(28)-Ru(4) | 72.5(2) |
| C(27)-C(28)-Ru(4) | 70.1(2) |
| C(29)-C(28)-H(28) | 126.4 |
| C(27)-C(28)-H(28) | 126.4 |
| Ru(4)-C(28)-H(28) | 126.4 |
| C(25)-C(29)-C(28) | 108.8(4) |
| C(25)-C(29)-Ru(4) | 71.0(2) |
| C(28)-C(29)-Ru(4) | 70.6(2) |
| C(25)-C(29)-H(29) | 125.6 |
| C(28)-C(29)-H(29) | 125.6 |

| | |
|---|---|
| Ru(4)-C(29)-H(29) | 125.6 |
| O(7)-C(30)-Ru(4) | 174.4(4) |
| O(8)-C(31)-Ru(4) | 175.6(4) |
| N(4)-C(32)-C(32)#4 | 111.6(4) |
| N(4)-C(32)-H(32A) | 109.3 |
| C(32)#4-C(32)-H(32A) | 109.3 |
| N(4)-C(32)-H(32B) | 109.3 |
| C(32)#4-C(32)-H(32B) | 109.3 |
| H(32A)-C(32)-H(32B) | 108.0 |
| F(2)-B(1)-F(4) | 113.7(5) |
| F(2)-B(1)-F(3) | 109.0(4) |
| F(4)-B(1)-F(3) | 108.1(5) |
| F(2)-B(1)-F(1) | 110.3(4) |
| F(4)-B(1)-F(1) | 107.3(4) |
| F(3)-B(1)-F(1) | 108.3(4) |
| F(7)-B(2)-F(6) | 111.0(4) |
| F(7)-B(2)-F(8) | 108.8(4) |
| F(6)-B(2)-F(8) | 109.7(4) |
| F(7)-B(2)-F(5) | 110.1(4) |
| F(6)-B(2)-F(5) | 109.6(4) |
| F(8)-B(2)-F(5) | 107.5(3) |
| F(12)-B(3)-F(10) | 109.8(4) |
| F(12)-B(3)-F(9) | 110.6(4) |
| F(10)-B(3)-F(9) | 109.4(4) |
| F(12)-B(3)-F(11) | 108.8(4) |
| F(10)-B(3)-F(11) | 107.6(4) |
| F(9)-B(3)-F(11) | 110.6(4) |
| F(15)-B(4)-F(16) | 110.3(4) |
| F(15)-B(4)-F(14) | 108.8(3) |
| F(16)-B(4)-F(14) | 111.2(4) |
| F(15)-B(4)-F(13) | 108.7(4) |
| F(16)-B(4)-F(13) | 108.4(3) |
| F(14)-B(4)-F(13) | 109.4(4) |
| C(8)-N(1)-Ru(1) | 119.2(2) |
| C(8)-N(1)-H(1A) | 107.5 |
| Ru(1)-N(1)-H(1A) | 107.5 |
| C(8)-N(1)-H(1B) | 107.5 |
| Ru(1)-N(1)-H(1B) | 107.5 |

| | |
|---|---|
| H(1A)-N(1)-H(1B) | 107.0 |
| C(16)-N(2)-Ru(2) | 119.7(2) |
| C(16)-N(2)-H(2A) | 107.4 |
| Ru(2)-N(2)-H(2A) | 107.4 |
| C(16)-N(2)-H(2B) | 107.4 |
| Ru(2)-N(2)-H(2B) | 107.4 |
| H(2A)-N(2)-H(2B) | 106.9 |
| C(24)-N(3)-Ru(3) | 116.2(2) |
| C(24)-N(3)-H(3A) | 108.2 |
| Ru(3)-N(3)-H(3A) | 108.2 |
| C(24)-N(3)-H(3B) | 108.2 |
| Ru(3)-N(3)-H(3B) | 108.2 |
| H(3A)-N(3)-H(3B) | 107.4 |
| C(32)-N(4)-Ru(4) | 118.7(2) |
| C(32)-N(4)-H(4A) | 107.6 |
| Ru(4)-N(4)-H(4A) | 107.6 |
| C(32)-N(4)-H(4B) | 107.6 |
| Ru(4)-N(4)-H(4B) | 107.6 |
| H(4A)-N(4)-H(4B) | 107.1 |
| C(6)-Ru(1)-C(7) | 88.53(16) |
| C(6)-Ru(1)-N(1) | 92.74(14) |
| C(7)-Ru(1)-N(1) | 93.35(13) |
| C(6)-Ru(1)-C(4) | 120.45(15) |
| C(7)-Ru(1)-C(4) | 94.66(15) |
| N(1)-Ru(1)-C(4) | 145.98(13) |
| C(6)-Ru(1)-C(5) | 92.71(16) |
| C(7)-Ru(1)-C(5) | 121.34(15) |
| N(1)-Ru(1)-C(5) | 144.99(13) |
| C(4)-Ru(1)-C(5) | 37.56(16) |
| C(6)-Ru(1)-C(1) | 99.77(16) |
| C(7)-Ru(1)-C(1) | 157.19(15) |
| N(1)-Ru(1)-C(1) | 107.31(13) |
| C(4)-Ru(1)-C(1) | 62.79(15) |
| C(5)-Ru(1)-C(1) | 37.73(15) |
| C(6)-Ru(1)-C(3) | 155.40(15) |
| C(7)-Ru(1)-C(3) | 102.49(16) |
| N(1)-Ru(1)-C(3) | 108.27(13) |
| C(4)-Ru(1)-C(3) | 37.72(15) |

| | |
|---|---|
| C(5)-Ru(1)-C(3) | 62.74(16) |
| C(1)-Ru(1)-C(3) | 62.36(16) |
| C(6)-Ru(1)-C(2) | 133.80(16) |
| C(7)-Ru(1)-C(2) | 137.31(16) |
| N(1)-Ru(1)-C(2) | 90.26(13) |
| C(4)-Ru(1)-C(2) | 62.13(14) |
| C(5)-Ru(1)-C(2) | 61.80(15) |
| C(1)-Ru(1)-C(2) | 36.47(16) |
| C(3)-Ru(1)-C(2) | 37.17(15) |
| C(15)-Ru(2)-C(14) | 93.11(16) |
| C(15)-Ru(2)-N(2) | 91.34(14) |
| C(14)-Ru(2)-N(2) | 92.23(13) |
| C(15)-Ru(2)-C(13) | 93.19(16) |
| C(14)-Ru(2)-C(13) | 121.64(19) |
| N(2)-Ru(2)-C(13) | 145.47(17) |
| C(15)-Ru(2)-C(9) | 119.13(15) |
| C(14)-Ru(2)-C(9) | 91.88(16) |
| N(2)-Ru(2)-C(9) | 148.95(14) |
| C(13)-Ru(2)-C(9) | 37.18(18) |
| C(15)-Ru(2)-C(12) | 102.01(17) |
| C(14)-Ru(2)-C(12) | 153.95(17) |
| N(2)-Ru(2)-C(12) | 108.30(15) |
| C(13)-Ru(2)-C(12) | 37.40(19) |
| C(9)-Ru(2)-C(12) | 62.26(17) |
| C(15)-Ru(2)-C(10) | 154.94(15) |
| C(14)-Ru(2)-C(10) | 96.50(16) |
| N(2)-Ru(2)-C(10) | 111.28(13) |
| C(13)-Ru(2)-C(10) | 62.12(16) |
| C(9)-Ru(2)-C(10) | 37.67(14) |
| C(12)-Ru(2)-C(10) | 61.59(16) |
| C(15)-Ru(2)-C(11) | 136.71(16) |
| C(14)-Ru(2)-C(11) | 129.74(16) |
| N(2)-Ru(2)-C(11) | 92.61(13) |
| C(13)-Ru(2)-C(11) | 61.58(16) |
| C(9)-Ru(2)-C(11) | 61.76(15) |
| C(12)-Ru(2)-C(11) | 36.60(17) |
| C(10)-Ru(2)-C(11) | 36.38(15) |
| C(22)-Ru(3)-C(23) | 90.41(19) |

| | |
|---|---|
| C(22)-Ru(3)-N(3) | 91.04(15) |
| C(23)-Ru(3)-N(3) | 91.80(15) |
| C(22)-Ru(3)-C(20) | 121.97(17) |
| C(23)-Ru(3)-C(20) | 92.57(18) |
| N(3)-Ru(3)-C(20) | 146.65(15) |
| C(22)-Ru(3)-C(19) | 95.46(17) |
| C(23)-Ru(3)-C(19) | 120.7(2) |
| N(3)-Ru(3)-C(19) | 146.69(18) |
| C(20)-Ru(3)-C(19) | 37.00(19) |
| C(22)-Ru(3)-C(21) | 157.34(17) |
| C(23)-Ru(3)-C(21) | 98.57(18) |
| N(3)-Ru(3)-C(21) | 109.31(14) |
| C(20)-Ru(3)-C(21) | 37.38(16) |
| C(19)-Ru(3)-C(21) | 62.07(17) |
| C(22)-Ru(3)-C(18) | 102.78(19) |
| C(23)-Ru(3)-C(18) | 154.86(19) |
| N(3)-Ru(3)-C(18) | 109.01(18) |
| C(20)-Ru(3)-C(18) | 62.29(18) |
| C(19)-Ru(3)-C(18) | 37.7(2) |
| C(21)-Ru(3)-C(18) | 61.86(18) |
| C(22)-Ru(3)-C(17) | 136.9(2) |
| C(23)-Ru(3)-C(17) | 132.5(2) |
| N(3)-Ru(3)-C(17) | 91.72(15) |
| C(20)-Ru(3)-C(17) | 61.68(16) |
| C(19)-Ru(3)-C(17) | 61.8(2) |
| C(21)-Ru(3)-C(17) | 36.65(17) |
| C(18)-Ru(3)-C(17) | 36.7(2) |
| C(30)-Ru(4)-C(31) | 94.74(17) |
| C(30)-Ru(4)-N(4) | 91.22(15) |
| C(31)-Ru(4)-N(4) | 91.18(15) |
| C(30)-Ru(4)-C(26) | 92.37(18) |
| C(31)-Ru(4)-C(26) | 116.55(16) |
| N(4)-Ru(4)-C(26) | 151.59(14) |
| C(30)-Ru(4)-C(27) | 123.27(18) |
| C(31)-Ru(4)-C(27) | 91.54(17) |
| N(4)-Ru(4)-C(27) | 145.01(16) |
| C(26)-Ru(4)-C(27) | 37.09(18) |
| C(30)-Ru(4)-C(28) | 154.12(18) |

| | |
|---|---|
| C(31)-Ru(4)-C(28) | 101.89(17) |
| N(4)-Ru(4)-C(28) | 107.94(15) |
| C(26)-Ru(4)-C(28) | 62.50(18) |
| C(27)-Ru(4)-C(28) | 37.64(18) |
| C(30)-Ru(4)-C(25) | 94.73(17) |
| C(31)-Ru(4)-C(25) | 152.93(16) |
| N(4)-Ru(4)-C(25) | 113.90(13) |
| C(26)-Ru(4)-C(25) | 37.71(15) |
| C(27)-Ru(4)-C(25) | 62.21(16) |
| C(28)-Ru(4)-C(25) | 61.96(16) |
| C(30)-Ru(4)-C(29) | 127.15(16) |
| C(31)-Ru(4)-C(29) | 137.58(17) |
| N(4)-Ru(4)-C(29) | 93.94(14) |
| C(26)-Ru(4)-C(29) | 61.90(16) |
| C(27)-Ru(4)-C(29) | 61.88(16) |
| C(28)-Ru(4)-C(29) | 36.97(15) |
| C(25)-Ru(4)-C(29) | 36.46(16) |

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Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z  #2 -x+2,-y,-z+1  #3 -x+1,-y+1,-z

#4 -x+1,-y,-z+1

**Table B50:** Anisotropic displacement parameters ($Å^2 x\ 10^3$)for {[$\eta^5$-$C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 50(2) | 28(2) | 16(2) | 5(2) | -5(2) | 7(2) |
| C(2) | 44(2) | 32(2) | 21(2) | -2(2) | -9(2) | 20(2) |
| C(3) | 31(2) | 36(2) | 24(2) | -4(2) | -10(2) | 9(2) |
| C(4) | 38(2) | 28(2) | 17(2) | -5(1) | -8(2) | 10(2) |
| C(5) | 46(2) | 36(2) | 12(2) | 0(2) | 1(2) | 13(2) |
| C(6) | 29(2) | 24(2) | 16(2) | 2(1) | 2(1) | 6(1) |
| C(7) | 26(2) | 24(2) | 16(2) | -4(1) | 0(1) | 6(1) |
| C(8) | 24(2) | 22(2) | 13(2) | 0(1) | 1(1) | 5(1) |
| C(9) | 54(3) | 33(2) | 17(2) | 4(2) | 3(2) | 19(2) |
| C(10) | 39(2) | 26(2) | 20(2) | 0(1) | 4(2) | 8(2) |
| C(11) | 39(2) | 37(2) | 18(2) | 1(2) | 9(2) | 16(2) |
| C(12) | 36(2) | 56(3) | 26(2) | -3(2) | 17(2) | -2(2) |
| C(13) | 76(3) | 28(2) | 20(2) | 5(2) | 18(2) | -1(2) |
| C(14) | 34(2) | 23(2) | 19(2) | 1(1) | -1(1) | 7(2) |
| C(15) | 31(2) | 23(2) | 21(2) | 6(1) | 7(1) | 5(2) |
| C(16) | 24(2) | 22(2) | 15(2) | 0(1) | 4(1) | 7(1) |
| C(17) | 44(3) | 25(2) | 62(3) | 2(2) | 29(2) | 0(2) |
| C(18) | 33(2) | 37(3) | 83(4) | 23(3) | 0(2) | 2(2) |
| C(19) | 62(3) | 31(2) | 38(2) | 5(2) | -10(2) | -20(2) |
| C(20) | 48(3) | 20(2) | 45(3) | 1(2) | 16(2) | 4(2) |
| C(21) | 40(2) | 25(2) | 33(2) | 3(2) | 5(2) | 0(2) |
| C(22) | 35(2) | 31(2) | 23(2) | -3(2) | 0(2) | -3(2) |
| C(23) | 31(2) | 34(2) | 31(2) | -9(2) | 7(2) | 3(2) |
| C(24) | 22(2) | 22(2) | 19(2) | 2(1) | -1(1) | 5(1) |
| C(25) | 43(2) | 30(2) | 24(2) | 4(2) | 1(2) | 6(2) |
| C(26) | 51(3) | 31(2) | 32(2) | 8(2) | 12(2) | 11(2) |
| C(27) | 63(3) | 35(2) | 23(2) | 4(2) | -1(2) | 21(2) |
| C(28) | 40(2) | 42(3) | 34(2) | -3(2) | -4(2) | 16(2) |
| C(29) | 43(2) | 27(2) | 26(2) | 0(2) | 7(2) | 10(2) |
| C(30) | 29(2) | 34(2) | 19(2) | 0(2) | 3(1) | 3(2) |
| C(31) | 29(2) | 32(2) | 24(2) | 6(2) | 4(2) | 1(2) |
| C(32) | 21(2) | 30(2) | 19(2) | 3(2) | 1(1) | 2(1) |
| B(1) | 26(2) | 29(2) | 41(3) | -1(2) | 3(2) | 2(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| B(2) | 33(2) | 30(2) | 28(2) | 6(2) | -4(2) | 7(2) |
| B(3) | 27(2) | 43(3) | 30(2) | -12(2) | -3(2) | 13(2) |
| B(4) | 27(2) | 29(2) | 36(2) | 4(2) | 9(2) | 8(2) |
| N(1) | 25(2) | 21(2) | 14(1) | -2(1) | 1(1) | 7(1) |
| N(2) | 25(2) | 22(2) | 16(1) | 2(1) | 6(1) | 8(1) |
| N(3) | 25(2) | 22(2) | 20(1) | 0(1) | -1(1) | 6(1) |
| N(4) | 24(2) | 32(2) | 23(2) | 6(1) | 5(1) | 6(1) |
| O(1) | 36(2) | 25(1) | 29(1) | 6(1) | 3(1) | 9(1) |
| O(2) | 26(2) | 42(2) | 38(2) | 2(1) | 2(1) | 6(1) |
| O(3) | 44(2) | 23(1) | 30(2) | -1(1) | 5(1) | 2(1) |
| O(4) | 26(2) | 35(2) | 37(2) | 1(1) | 2(1) | 6(1) |
| O(5) | 28(2) | 65(2) | 53(2) | -22(2) | 5(1) | 10(2) |
| O(6) | 61(2) | 49(2) | 23(2) | 8(1) | 3(1) | -3(2) |
| O(7) | 28(2) | 51(2) | 32(2) | -7(1) | 0(1) | 5(1) |
| O(8) | 46(2) | 42(2) | 25(2) | -2(1) | 1(1) | -5(1) |
| F(1) | 40(2) | 38(2) | 69(2) | -5(1) | 24(1) | 0(1) |
| F(2) | 63(2) | 136(4) | 65(2) | 54(2) | -3(2) | 7(2) |
| F(3) | 87(3) | 104(3) | 52(2) | 8(2) | -1(2) | -58(2) |
| F(4) | 75(2) | 72(2) | 105(3) | 15(2) | 50(2) | 40(2) |
| F(5) | 29(1) | 38(1) | 35(1) | 3(1) | 5(1) | -3(1) |
| F(6) | 58(2) | 53(2) | 43(2) | 6(1) | -25(1) | 5(1) |
| F(7) | 45(2) | 29(1) | 57(2) | 1(1) | -5(1) | 11(1) |
| F(8) | 37(1) | 46(2) | 33(1) | 14(1) | 9(1) | 11(1) |
| F(9) | 47(2) | 68(2) | 45(2) | -7(1) | -10(1) | 34(2) |
| F(10) | 39(2) | 49(2) | 64(2) | 7(1) | 16(1) | 6(1) |
| F(11) | 33(1) | 90(2) | 59(2) | -47(2) | -15(1) | 29(2) |
| F(12) | 30(1) | 37(1) | 42(1) | 2(1) | -2(1) | 4(1) |
| F(13) | 29(1) | 29(1) | 56(2) | 6(1) | 7(1) | 6(1) |
| F(14) | 30(1) | 51(2) | 33(1) | 6(1) | -1(1) | 15(1) |
| F(15) | 34(1) | 39(1) | 43(1) | 1(1) | -4(1) | 10(1) |
| F(16) | 55(2) | 40(2) | 51(2) | 4(1) | 31(1) | 5(1) |
| Ru(1) | 23(1) | 17(1) | 12(1) | -1(1) | 0(1) | 6(1) |
| Ru(2) | 26(1) | 17(1) | 16(1) | 2(1) | 5(1) | 5(1) |
| Ru(3) | 24(1) | 20(1) | 17(1) | -1(1) | 3(1) | 3(1) |
| Ru(4) | 26(1) | 29(1) | 17(1) | 3(1) | 3(1) | 5(1) |

**Table B51:** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 9363 | 4355 | 3904 | 37 |
| H(2) | 11380 | 4724 | 3263 | 38 |
| H(3) | 12024 | 6598 | 3338 | 37 |
| H(4) | 10354 | 7387 | 4048 | 33 |
| H(5) | 8724 | 6004 | 4401 | 37 |
| H(8A) | 10424 | 5980 | 339 | 24 |
| H(8B) | 9087 | 5505 | 273 | 24 |
| H(9) | 8649 | 1087 | 653 | 40 |
| H(10) | 8968 | -667 | 1025 | 33 |
| H(11) | 11088 | -580 | 1660 | 36 |
| H(12) | 12090 | 1206 | 1691 | 48 |
| H(13) | 10572 | 2231 | 1065 | 50 |
| H(16A) | 8955 | 246 | 4568 | 24 |
| H(16B) | 10106 | 1014 | 4833 | 24 |
| H(17) | 6339 | 7788 | -407 | 52 |
| H(18) | 7136 | 7741 | 1328 | 61 |
| H(19) | 6037 | 8832 | 2376 | 57 |
| H(20) | 4585 | 9526 | 1287 | 45 |
| H(21) | 4764 | 8882 | -438 | 39 |
| H(24A) | 5029 | 5223 | 1004 | 25 |
| H(24B) | 5938 | 5754 | 319 | 25 |
| H(25) | 6317 | 4148 | 5555 | 39 |
| H(26) | 6701 | 4447 | 3784 | 44 |
| H(27) | 4791 | 3922 | 2777 | 47 |
| H(28) | 3198 | 3273 | 3905 | 46 |
| H(29) | 4164 | 3423 | 5621 | 37 |
| H(32A) | 6068 | 475 | 4673 | 28 |
| H(32B) | 4903 | 172 | 4007 | 28 |
| H(1A) | 10784 | 4913 | 1434 | 24 |
| H(1B) | 9571 | 4416 | 1347 | 24 |
| H(2A) | 9989 | -548 | 3532 | 24 |
| H(2B) | 11038 | 178 | 3767 | 24 |

| | | | | |
|---|---|---|---|---|
| H(3A) | 3591 | 5843 | 194 | 27 |
| H(3B) | 4403 | 6300 | -480 | 27 |
| H(4A) | 5095 | 1488 | 5554 | 31 |
| H(4B) | 4054 | 1234 | 4892 | 31 |

**Table B52:** Torsion angles [°] for $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$.

| | |
|---|---|
| C(5)-C(1)-C(2)-C(3) | -1.3(4) |
| Ru(1)-C(1)-C(2)-C(3) | 60.6(3) |
| C(5)-C(1)-C(2)-Ru(1) | -61.9(3) |
| C(1)-C(2)-C(3)-C(4) | 1.1(4) |
| Ru(1)-C(2)-C(3)-C(4) | 61.7(2) |
| C(1)-C(2)-C(3)-Ru(1) | -60.6(3) |
| C(2)-C(3)-C(4)-C(5) | -0.5(4) |
| Ru(1)-C(3)-C(4)-C(5) | 62.6(3) |
| C(2)-C(3)-C(4)-Ru(1) | -63.1(3) |
| C(3)-C(4)-C(5)-C(1) | -0.3(4) |
| Ru(1)-C(4)-C(5)-C(1) | 63.1(3) |
| C(3)-C(4)-C(5)-Ru(1) | -63.4(3) |
| C(2)-C(1)-C(5)-C(4) | 1.0(4) |
| Ru(1)-C(1)-C(5)-C(4) | -62.5(3) |
| C(2)-C(1)-C(5)-Ru(1) | 63.5(3) |
| C(13)-C(9)-C(10)-C(11) | -0.2(4) |
| Ru(2)-C(9)-C(10)-C(11) | -63.4(3) |
| C(13)-C(9)-C(10)-Ru(2) | 63.2(3) |
| C(9)-C(10)-C(11)-C(12) | 0.7(4) |
| Ru(2)-C(10)-C(11)-C(12) | -60.8(3) |
| C(9)-C(10)-C(11)-Ru(2) | 61.4(3) |
| C(10)-C(11)-C(12)-C(13) | -0.9(4) |
| Ru(2)-C(11)-C(12)-C(13) | -61.7(3) |
| C(10)-C(11)-C(12)-Ru(2) | 60.8(3) |
| C(10)-C(9)-C(13)-C(12) | -0.3(4) |
| Ru(2)-C(9)-C(13)-C(12) | 63.6(3) |
| C(10)-C(9)-C(13)-Ru(2) | -63.9(3) |
| C(11)-C(12)-C(13)-C(9) | 0.7(5) |
| Ru(2)-C(12)-C(13)-C(9) | -62.8(3) |

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| C(11)-C(12)-C(13)-Ru(2) | 63.6(3) |
| C(21)-C(17)-C(18)-C(19) | -1.1(5) |
| Ru(3)-C(17)-C(18)-C(19) | -62.0(3) |
| C(21)-C(17)-C(18)-Ru(3) | 60.9(3) |
| C(17)-C(18)-C(19)-C(20) | 0.8(5) |
| Ru(3)-C(18)-C(19)-C(20) | -62.8(3) |
| C(17)-C(18)-C(19)-Ru(3) | 63.5(3) |
| C(18)-C(19)-C(20)-C(21) | -0.1(5) |
| Ru(3)-C(19)-C(20)-C(21) | -63.3(3) |
| C(18)-C(19)-C(20)-Ru(3) | 63.2(3) |
| C(18)-C(17)-C(21)-C(20) | 1.0(5) |
| Ru(3)-C(17)-C(21)-C(20) | 62.0(3) |
| C(18)-C(17)-C(21)-Ru(3) | -61.0(3) |
| C(19)-C(20)-C(21)-C(17) | -0.5(5) |
| Ru(3)-C(20)-C(21)-C(17) | -63.4(3) |
| C(19)-C(20)-C(21)-Ru(3) | 62.9(3) |
| C(29)-C(25)-C(26)-C(27) | 0.4(5) |
| Ru(4)-C(25)-C(26)-C(27) | 63.4(3) |
| C(29)-C(25)-C(26)-Ru(4) | -63.0(3) |
| C(25)-C(26)-C(27)-C(28) | -1.1(5) |
| Ru(4)-C(26)-C(27)-C(28) | 63.0(3) |
| C(25)-C(26)-C(27)-Ru(4) | -64.0(3) |
| C(26)-C(27)-C(28)-C(29) | 1.3(5) |
| Ru(4)-C(27)-C(28)-C(29) | 63.6(3) |
| C(26)-C(27)-C(28)-Ru(4) | -62.3(3) |
| C(26)-C(25)-C(29)-C(28) | 0.4(5) |
| Ru(4)-C(25)-C(29)-C(28) | -60.7(3) |
| C(26)-C(25)-C(29)-Ru(4) | 61.1(3) |
| C(27)-C(28)-C(29)-C(25) | -1.0(5) |
| Ru(4)-C(28)-C(29)-C(25) | 61.0(3) |
| C(27)-C(28)-C(29)-Ru(4) | -62.0(3) |
| C(8)#1-C(8)-N(1)-Ru(1) | -176.3(3) |
| C(16)#2-C(16)-N(2)-Ru(2) | 178.7(3) |
| C(24)#3-C(24)-N(3)-Ru(3) | -177.1(3) |
| C(32)#4-C(32)-N(4)-Ru(4) | 176.7(3) |
| O(2)-C(6)-Ru(1)-C(7) | -94(4) |
| O(2)-C(6)-Ru(1)-N(1) | 173(4) |
| O(2)-C(6)-Ru(1)-C(4) | 0(4) |

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| O(2)-C(6)-Ru(1)-C(5) | 27(4) |
| O(2)-C(6)-Ru(1)-C(1) | 65(4) |
| O(2)-C(6)-Ru(1)-C(3) | 24(4) |
| O(2)-C(6)-Ru(1)-C(2) | 80(4) |
| O(1)-C(7)-Ru(1)-C(6) | 46(5) |
| O(1)-C(7)-Ru(1)-N(1) | 139(5) |
| O(1)-C(7)-Ru(1)-C(4) | -74(5) |
| O(1)-C(7)-Ru(1)-C(5) | -46(5) |
| O(1)-C(7)-Ru(1)-C(1) | -66(5) |
| O(1)-C(7)-Ru(1)-C(3) | -111(5) |
| O(1)-C(7)-Ru(1)-C(2) | -127(5) |
| C(8)-N(1)-Ru(1)-C(6) | 73.0(3) |
| C(8)-N(1)-Ru(1)-C(7) | -15.7(3) |
| C(8)-N(1)-Ru(1)-C(4) | -119.2(3) |
| C(8)-N(1)-Ru(1)-C(5) | 171.6(3) |
| C(8)-N(1)-Ru(1)-C(1) | 174.1(3) |
| C(8)-N(1)-Ru(1)-C(3) | -120.1(3) |
| C(8)-N(1)-Ru(1)-C(2) | -153.2(3) |
| C(5)-C(4)-Ru(1)-C(6) | 47.6(3) |
| C(3)-C(4)-Ru(1)-C(6) | 164.5(2) |
| C(5)-C(4)-Ru(1)-C(7) | 138.6(2) |
| C(3)-C(4)-Ru(1)-C(7) | -104.4(3) |
| C(5)-C(4)-Ru(1)-N(1) | -118.4(3) |
| C(3)-C(4)-Ru(1)-N(1) | -1.4(4) |
| C(3)-C(4)-Ru(1)-C(5) | 117.0(3) |
| C(5)-C(4)-Ru(1)-C(1) | -37.8(2) |
| C(3)-C(4)-Ru(1)-C(1) | 79.2(3) |
| C(5)-C(4)-Ru(1)-C(3) | -117.0(3) |
| C(5)-C(4)-Ru(1)-C(2) | -79.1(3) |
| C(3)-C(4)-Ru(1)-C(2) | 37.8(2) |
| C(4)-C(5)-Ru(1)-C(6) | -140.4(2) |
| C(1)-C(5)-Ru(1)-C(6) | 102.5(3) |
| C(4)-C(5)-Ru(1)-C(7) | -50.5(3) |
| C(1)-C(5)-Ru(1)-C(7) | -167.6(2) |
| C(4)-C(5)-Ru(1)-N(1) | 120.9(3) |
| C(1)-C(5)-Ru(1)-N(1) | 3.8(4) |
| C(1)-C(5)-Ru(1)-C(4) | -117.1(4) |
| C(4)-C(5)-Ru(1)-C(1) | 117.1(4) |

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| C(4)-C(5)-Ru(1)-C(3) | 37.8(2) |
| C(1)-C(5)-Ru(1)-C(3) | -79.2(3) |
| C(4)-C(5)-Ru(1)-C(2) | 80.0(3) |
| C(1)-C(5)-Ru(1)-C(2) | -37.0(3) |
| C(2)-C(1)-Ru(1)-C(6) | 161.6(2) |
| C(5)-C(1)-Ru(1)-C(6) | -81.7(3) |
| C(2)-C(1)-Ru(1)-C(7) | -88.4(5) |
| C(5)-C(1)-Ru(1)-C(7) | 28.3(5) |
| C(2)-C(1)-Ru(1)-N(1) | 65.6(3) |
| C(5)-C(1)-Ru(1)-N(1) | -177.7(2) |
| C(2)-C(1)-Ru(1)-C(4) | -79.1(3) |
| C(5)-C(1)-Ru(1)-C(4) | 37.6(3) |
| C(2)-C(1)-Ru(1)-C(5) | -116.7(4) |
| C(2)-C(1)-Ru(1)-C(3) | -36.4(2) |
| C(5)-C(1)-Ru(1)-C(3) | 80.3(3) |
| C(5)-C(1)-Ru(1)-C(2) | 116.7(4) |
| C(2)-C(3)-Ru(1)-C(6) | 82.6(4) |
| C(4)-C(3)-Ru(1)-C(6) | -33.5(5) |
| C(2)-C(3)-Ru(1)-C(7) | -162.5(2) |
| C(4)-C(3)-Ru(1)-C(7) | 81.3(3) |
| C(2)-C(3)-Ru(1)-N(1) | -64.7(3) |
| C(4)-C(3)-Ru(1)-N(1) | 179.2(2) |
| C(2)-C(3)-Ru(1)-C(4) | 116.1(4) |
| C(2)-C(3)-Ru(1)-C(5) | 78.5(3) |
| C(4)-C(3)-Ru(1)-C(5) | -37.7(2) |
| C(2)-C(3)-Ru(1)-C(1) | 35.7(2) |
| C(4)-C(3)-Ru(1)-C(1) | -80.4(3) |
| C(4)-C(3)-Ru(1)-C(2) | -116.1(4) |
| C(1)-C(2)-Ru(1)-C(6) | -25.6(3) |
| C(3)-C(2)-Ru(1)-C(6) | -145.1(3) |
| C(1)-C(2)-Ru(1)-C(7) | 145.1(3) |
| C(3)-C(2)-Ru(1)-C(7) | 25.6(3) |
| C(1)-C(2)-Ru(1)-N(1) | -119.6(2) |
| C(3)-C(2)-Ru(1)-N(1) | 120.8(2) |
| C(1)-C(2)-Ru(1)-C(4) | 81.1(3) |
| C(3)-C(2)-Ru(1)-C(4) | -38.4(2) |
| C(1)-C(2)-Ru(1)-C(5) | 38.3(2) |
| C(3)-C(2)-Ru(1)-C(5) | -81.2(3) |

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| C(3)-C(2)-Ru(1)-C(1) | -119.5(3) |
| C(1)-C(2)-Ru(1)-C(3) | 119.5(3) |
| O(3)-C(15)-Ru(2)-C(14) | -118(6) |
| O(3)-C(15)-Ru(2)-N(2) | 149(6) |
| O(3)-C(15)-Ru(2)-C(13) | 4(6) |
| O(3)-C(15)-Ru(2)-C(9) | -25(6) |
| O(3)-C(15)-Ru(2)-C(12) | 40(6) |
| O(3)-C(15)-Ru(2)-C(10) | -6(6) |
| O(3)-C(15)-Ru(2)-C(11) | 54(6) |
| O(4)-C(14)-Ru(2)-C(15) | 128(4) |
| O(4)-C(14)-Ru(2)-N(2) | -141(4) |
| O(4)-C(14)-Ru(2)-C(13) | 32(4) |
| O(4)-C(14)-Ru(2)-C(9) | 9(4) |
| O(4)-C(14)-Ru(2)-C(12) | 2(4) |
| O(4)-C(14)-Ru(2)-C(10) | -29(4) |
| O(4)-C(14)-Ru(2)-C(11) | -45(4) |
| C(16)-N(2)-Ru(2)-C(15) | 46.8(3) |
| C(16)-N(2)-Ru(2)-C(14) | -46.4(3) |
| C(16)-N(2)-Ru(2)-C(13) | 144.4(3) |
| C(16)-N(2)-Ru(2)-C(9) | -143.8(3) |
| C(16)-N(2)-Ru(2)-C(12) | 149.9(3) |
| C(16)-N(2)-Ru(2)-C(10) | -144.3(3) |
| C(16)-N(2)-Ru(2)-C(11) | -176.4(3) |
| C(9)-C(13)-Ru(2)-C(15) | -137.2(3) |
| C(12)-C(13)-Ru(2)-C(15) | 105.7(3) |
| C(9)-C(13)-Ru(2)-C(14) | -41.5(3) |
| C(12)-C(13)-Ru(2)-C(14) | -158.7(3) |
| C(9)-C(13)-Ru(2)-N(2) | 125.8(3) |
| C(12)-C(13)-Ru(2)-N(2) | 8.7(4) |
| C(12)-C(13)-Ru(2)-C(9) | -117.2(4) |
| C(9)-C(13)-Ru(2)-C(12) | 117.2(4) |
| C(9)-C(13)-Ru(2)-C(10) | 38.4(2) |
| C(12)-C(13)-Ru(2)-C(10) | -78.8(3) |
| C(9)-C(13)-Ru(2)-C(11) | 79.8(3) |
| C(12)-C(13)-Ru(2)-C(11) | -37.3(3) |
| C(13)-C(9)-Ru(2)-C(15) | 51.0(3) |
| C(10)-C(9)-Ru(2)-C(15) | 167.2(2) |
| C(13)-C(9)-Ru(2)-C(14) | 145.6(3) |

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| C(10)-C(9)-Ru(2)-C(14) | -98.2(3) |
| C(13)-C(9)-Ru(2)-N(2) | -116.9(3) |
| C(10)-C(9)-Ru(2)-N(2) | -0.8(4) |
| C(10)-C(9)-Ru(2)-C(13) | 116.2(4) |
| C(13)-C(9)-Ru(2)-C(12) | -37.6(3) |
| C(10)-C(9)-Ru(2)-C(12) | 78.5(3) |
| C(13)-C(9)-Ru(2)-C(10) | -116.2(4) |
| C(13)-C(9)-Ru(2)-C(11) | -79.3(3) |
| C(10)-C(9)-Ru(2)-C(11) | 36.9(2) |
| C(11)-C(12)-Ru(2)-C(15) | 164.1(3) |
| C(13)-C(12)-Ru(2)-C(15) | -79.4(3) |
| C(11)-C(12)-Ru(2)-C(14) | -71.8(5) |
| C(13)-C(12)-Ru(2)-C(14) | 44.8(5) |
| C(11)-C(12)-Ru(2)-N(2) | 68.6(3) |
| C(13)-C(12)-Ru(2)-N(2) | -174.8(2) |
| C(11)-C(12)-Ru(2)-C(13) | -116.6(4) |
| C(11)-C(12)-Ru(2)-C(9) | -79.1(3) |
| C(13)-C(12)-Ru(2)-C(9) | 37.4(3) |
| C(11)-C(12)-Ru(2)-C(10) | -36.2(2) |
| C(13)-C(12)-Ru(2)-C(10) | 80.3(3) |
| C(13)-C(12)-Ru(2)-C(11) | 116.6(4) |
| C(11)-C(10)-Ru(2)-C(15) | 89.7(4) |
| C(9)-C(10)-Ru(2)-C(15) | -27.2(5) |
| C(11)-C(10)-Ru(2)-C(14) | -158.5(2) |
| C(9)-C(10)-Ru(2)-C(14) | 84.6(3) |
| C(11)-C(10)-Ru(2)-N(2) | -63.5(3) |
| C(9)-C(10)-Ru(2)-N(2) | 179.6(2) |
| C(11)-C(10)-Ru(2)-C(13) | 79.1(3) |
| C(9)-C(10)-Ru(2)-C(13) | -37.8(3) |
| C(11)-C(10)-Ru(2)-C(9) | 116.9(4) |
| C(11)-C(10)-Ru(2)-C(12) | 36.4(3) |
| C(9)-C(10)-Ru(2)-C(12) | -80.5(3) |
| C(9)-C(10)-Ru(2)-C(11) | -116.9(4) |
| C(10)-C(11)-Ru(2)-C(15) | -141.9(3) |
| C(12)-C(11)-Ru(2)-C(15) | -23.0(4) |
| C(10)-C(11)-Ru(2)-C(14) | 28.3(3) |
| C(12)-C(11)-Ru(2)-C(14) | 147.2(3) |
| C(10)-C(11)-Ru(2)-N(2) | 123.4(2) |

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| C(12)-C(11)-Ru(2)-N(2) | -117.8(3) |
| C(10)-C(11)-Ru(2)-C(13) | -80.7(3) |
| C(12)-C(11)-Ru(2)-C(13) | 38.1(3) |
| C(10)-C(11)-Ru(2)-C(9) | -38.2(2) |
| C(12)-C(11)-Ru(2)-C(9) | 80.6(3) |
| C(10)-C(11)-Ru(2)-C(12) | -118.8(4) |
| C(12)-C(11)-Ru(2)-C(10) | 118.8(4) |
| O(6)-C(22)-Ru(3)-C(23) | -84(12) |
| O(6)-C(22)-Ru(3)-N(3) | -176(100) |
| O(6)-C(22)-Ru(3)-C(20) | 9(12) |
| O(6)-C(22)-Ru(3)-C(19) | 37(12) |
| O(6)-C(22)-Ru(3)-C(21) | 30(12) |
| O(6)-C(22)-Ru(3)-C(18) | 74(12) |
| O(6)-C(22)-Ru(3)-C(17) | 90(12) |
| O(5)-C(23)-Ru(3)-C(22) | 107(5) |
| O(5)-C(23)-Ru(3)-N(3) | -162(5) |
| O(5)-C(23)-Ru(3)-C(20) | -16(5) |
| O(5)-C(23)-Ru(3)-C(19) | 10(5) |
| O(5)-C(23)-Ru(3)-C(21) | -53(5) |
| O(5)-C(23)-Ru(3)-C(18) | -16(5) |
| O(5)-C(23)-Ru(3)-C(17) | -68(5) |
| C(24)-N(3)-Ru(3)-C(22) | -55.5(3) |
| C(24)-N(3)-Ru(3)-C(23) | -146.0(3) |
| C(24)-N(3)-Ru(3)-C(20) | 116.6(3) |
| C(24)-N(3)-Ru(3)-C(19) | 46.0(4) |
| C(24)-N(3)-Ru(3)-C(21) | 114.3(3) |
| C(24)-N(3)-Ru(3)-C(18) | 48.4(3) |
| C(24)-N(3)-Ru(3)-C(17) | 81.4(3) |
| C(19)-C(20)-Ru(3)-C(22) | 50.1(4) |
| C(21)-C(20)-Ru(3)-C(22) | 167.1(3) |
| C(19)-C(20)-Ru(3)-C(23) | 142.2(3) |
| C(21)-C(20)-Ru(3)-C(23) | -100.8(3) |
| C(19)-C(20)-Ru(3)-N(3) | -120.6(3) |
| C(21)-C(20)-Ru(3)-N(3) | -3.6(4) |
| C(21)-C(20)-Ru(3)-C(19) | 117.1(4) |
| C(19)-C(20)-Ru(3)-C(21) | -117.1(4) |
| C(19)-C(20)-Ru(3)-C(18) | -38.0(3) |
| C(21)-C(20)-Ru(3)-C(18) | 79.1(3) |

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| C(19)-C(20)-Ru(3)-C(17) | -79.8(3) |
| C(21)-C(20)-Ru(3)-C(17) | 37.3(3) |
| C(20)-C(19)-Ru(3)-C(22) | -139.2(3) |
| C(18)-C(19)-Ru(3)-C(22) | 103.9(3) |
| C(20)-C(19)-Ru(3)-C(23) | -45.5(4) |
| C(18)-C(19)-Ru(3)-C(23) | -162.4(3) |
| C(20)-C(19)-Ru(3)-N(3) | 120.5(3) |
| C(18)-C(19)-Ru(3)-N(3) | 3.6(4) |
| C(18)-C(19)-Ru(3)-C(20) | -116.9(4) |
| C(20)-C(19)-Ru(3)-C(21) | 37.7(3) |
| C(18)-C(19)-Ru(3)-C(21) | -79.2(3) |
| C(20)-C(19)-Ru(3)-C(18) | 116.9(4) |
| C(20)-C(19)-Ru(3)-C(17) | 79.5(3) |
| C(18)-C(19)-Ru(3)-C(17) | -37.5(3) |
| C(17)-C(21)-Ru(3)-C(22) | 87.4(5) |
| C(20)-C(21)-Ru(3)-C(22) | -29.3(6) |
| C(17)-C(21)-Ru(3)-C(23) | -160.3(3) |
| C(20)-C(21)-Ru(3)-C(23) | 83.0(3) |
| C(17)-C(21)-Ru(3)-N(3) | -65.3(3) |
| C(20)-C(21)-Ru(3)-N(3) | 177.9(3) |
| C(17)-C(21)-Ru(3)-C(20) | 116.7(4) |
| C(17)-C(21)-Ru(3)-C(19) | 79.4(3) |
| C(20)-C(21)-Ru(3)-C(19) | -37.3(3) |
| C(17)-C(21)-Ru(3)-C(18) | 36.4(3) |
| C(20)-C(21)-Ru(3)-C(18) | -80.3(3) |
| C(20)-C(21)-Ru(3)-C(17) | -116.7(4) |
| C(17)-C(18)-Ru(3)-C(22) | 161.5(3) |
| C(19)-C(18)-Ru(3)-C(22) | -82.3(3) |
| C(17)-C(18)-Ru(3)-C(23) | -78.5(6) |
| C(19)-C(18)-Ru(3)-C(23) | 37.7(6) |
| C(17)-C(18)-Ru(3)-N(3) | 65.9(3) |
| C(19)-C(18)-Ru(3)-N(3) | -177.9(3) |
| C(17)-C(18)-Ru(3)-C(20) | -78.9(3) |
| C(19)-C(18)-Ru(3)-C(20) | 37.3(3) |
| C(17)-C(18)-Ru(3)-C(19) | -116.2(4) |
| C(17)-C(18)-Ru(3)-C(21) | -36.4(3) |
| C(19)-C(18)-Ru(3)-C(21) | 79.8(3) |
| C(19)-C(18)-Ru(3)-C(17) | 116.2(4) |

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| C(21)-C(17)-Ru(3)-C(22) | -145.7(3) |
| C(18)-C(17)-Ru(3)-C(22) | -27.0(4) |
| C(21)-C(17)-Ru(3)-C(23) | 26.9(4) |
| C(18)-C(17)-Ru(3)-C(23) | 145.6(3) |
| C(21)-C(17)-Ru(3)-N(3) | 120.9(3) |
| C(18)-C(17)-Ru(3)-N(3) | -120.3(3) |
| C(21)-C(17)-Ru(3)-C(20) | -38.0(3) |
| C(18)-C(17)-Ru(3)-C(20) | 80.7(3) |
| C(21)-C(17)-Ru(3)-C(19) | -80.2(3) |
| C(18)-C(17)-Ru(3)-C(19) | 38.5(3) |
| C(18)-C(17)-Ru(3)-C(21) | 118.8(4) |
| C(21)-C(17)-Ru(3)-C(18) | -118.8(4) |
| O(7)-C(30)-Ru(4)-C(31) | 135(3) |
| O(7)-C(30)-Ru(4)-N(4) | -134(3) |
| O(7)-C(30)-Ru(4)-C(26) | 18(3) |
| O(7)-C(30)-Ru(4)-C(27) | 40(4) |
| O(7)-C(30)-Ru(4)-C(28) | 5(4) |
| O(7)-C(30)-Ru(4)-C(25) | -20(3) |
| O(7)-C(30)-Ru(4)-C(29) | -38(4) |
| O(8)-C(31)-Ru(4)-C(30) | -132(5) |
| O(8)-C(31)-Ru(4)-N(4) | 137(5) |
| O(8)-C(31)-Ru(4)-C(26) | -37(5) |
| O(8)-C(31)-Ru(4)-C(27) | -8(5) |
| O(8)-C(31)-Ru(4)-C(28) | 28(5) |
| O(8)-C(31)-Ru(4)-C(25) | -22(5) |
| O(8)-C(31)-Ru(4)-C(29) | 40(5) |
| C(32)-N(4)-Ru(4)-C(30) | -50.4(3) |
| C(32)-N(4)-Ru(4)-C(31) | 44.4(3) |
| C(32)-N(4)-Ru(4)-C(26) | -147.6(3) |
| C(32)-N(4)-Ru(4)-C(27) | 138.8(3) |
| C(32)-N(4)-Ru(4)-C(28) | 147.3(3) |
| C(32)-N(4)-Ru(4)-C(25) | -146.1(3) |
| C(32)-N(4)-Ru(4)-C(29) | -177.7(3) |
| C(27)-C(26)-Ru(4)-C(30) | 148.8(3) |
| C(25)-C(26)-Ru(4)-C(30) | -94.7(3) |
| C(27)-C(26)-Ru(4)-C(31) | 52.3(3) |
| C(25)-C(26)-Ru(4)-C(31) | 168.8(3) |
| C(27)-C(26)-Ru(4)-N(4) | -114.2(3) |

| | |
|---|---|
| C(25)-C(26)-Ru(4)-N(4) | 2.3(5) |
| C(25)-C(26)-Ru(4)-C(27) | 116.5(4) |
| C(27)-C(26)-Ru(4)-C(28) | -37.6(3) |
| C(25)-C(26)-Ru(4)-C(28) | 78.9(3) |
| C(27)-C(26)-Ru(4)-C(25) | -116.5(4) |
| C(27)-C(26)-Ru(4)-C(29) | -79.6(3) |
| C(25)-C(26)-Ru(4)-C(29) | 36.9(3) |
| C(26)-C(27)-Ru(4)-C(30) | -38.2(3) |
| C(28)-C(27)-Ru(4)-C(30) | -155.7(3) |
| C(26)-C(27)-Ru(4)-C(31) | -134.9(3) |
| C(28)-C(27)-Ru(4)-C(31) | 107.6(3) |
| C(26)-C(27)-Ru(4)-N(4) | 130.8(3) |
| C(28)-C(27)-Ru(4)-N(4) | 13.4(4) |
| C(28)-C(27)-Ru(4)-C(26) | -117.5(4) |
| C(26)-C(27)-Ru(4)-C(28) | 117.5(4) |
| C(26)-C(27)-Ru(4)-C(25) | 38.2(3) |
| C(28)-C(27)-Ru(4)-C(25) | -79.2(3) |
| C(26)-C(27)-Ru(4)-C(29) | 79.7(3) |
| C(28)-C(27)-Ru(4)-C(29) | -37.8(3) |
| C(29)-C(28)-Ru(4)-C(30) | -64.0(5) |
| C(27)-C(28)-Ru(4)-C(30) | 52.0(5) |
| C(29)-C(28)-Ru(4)-C(31) | 167.1(3) |
| C(27)-C(28)-Ru(4)-C(31) | -76.8(3) |
| C(29)-C(28)-Ru(4)-N(4) | 71.9(3) |
| C(27)-C(28)-Ru(4)-N(4) | -172.0(2) |
| C(29)-C(28)-Ru(4)-C(26) | -79.0(3) |
| C(27)-C(28)-Ru(4)-C(26) | 37.1(3) |
| C(29)-C(28)-Ru(4)-C(27) | -116.1(4) |
| C(29)-C(28)-Ru(4)-C(25) | -36.1(2) |
| C(27)-C(28)-Ru(4)-C(25) | 79.9(3) |
| C(27)-C(28)-Ru(4)-C(29) | 116.1(4) |
| C(29)-C(25)-Ru(4)-C(30) | -155.2(2) |
| C(26)-C(25)-Ru(4)-C(30) | 87.8(3) |
| C(29)-C(25)-Ru(4)-C(31) | 94.7(4) |
| C(26)-C(25)-Ru(4)-C(31) | -22.4(5) |
| C(29)-C(25)-Ru(4)-N(4) | -61.8(3) |
| C(26)-C(25)-Ru(4)-N(4) | -178.8(3) |
| C(29)-C(25)-Ru(4)-C(26) | 117.0(4) |

| | |
|---|---|
| C(29)-C(25)-Ru(4)-C(27) | 79.4(3) |
| C(26)-C(25)-Ru(4)-C(27) | -37.6(3) |
| C(29)-C(25)-Ru(4)-C(28) | 36.6(2) |
| C(26)-C(25)-Ru(4)-C(28) | -80.4(3) |
| C(26)-C(25)-Ru(4)-C(29) | -117.0(4) |
| C(25)-C(29)-Ru(4)-C(30) | 31.6(3) |
| C(28)-C(29)-Ru(4)-C(30) | 150.5(3) |
| C(25)-C(29)-Ru(4)-C(31) | -137.8(3) |
| C(28)-C(29)-Ru(4)-C(31) | -18.9(4) |
| C(25)-C(29)-Ru(4)-N(4) | 126.2(2) |
| C(28)-C(29)-Ru(4)-N(4) | -115.0(3) |
| C(25)-C(29)-Ru(4)-C(26) | -38.1(2) |
| C(28)-C(29)-Ru(4)-C(26) | 80.7(3) |
| C(25)-C(29)-Ru(4)-C(27) | -80.4(3) |
| C(28)-C(29)-Ru(4)-C(27) | 38.5(3) |
| C(25)-C(29)-Ru(4)-C(28) | -118.9(4) |
| C(28)-C(29)-Ru(4)-C(25) | 118.9(4) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z #2 -x+2,-y,-z+1 #3 -x+1,-y+1,-z

#4 -x+1,-y,-z+1

**Table B53:** Hydrogen bonds for $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$ [Å and °].

| D-H…A | [ARU] | D – H | | H...A | | D...A | | D - H...A |
|---|---|---|---|---|---|---|---|---|
| N(1) --H(1A) ..F(13) | [2566.08] | 0.92 | | 2.19 | | 3.072(4) | | 160 |
| N(1) --H(1B) ..F(5) | [2666.06] | 0.92 | | 2.13 | | 2.908(4) | | 142 |
| N(2) --H(2A) ..F(1) | [2656.05] | 0.92 | 2.03 | | 2.866(4) | | 150 | |
| N(2) --H(2B) ..F(11) | [2756.07] | 0.92 | 2.09 | | 2.960(4) | | 156 | |
| N(3) --H(3B) ..F(8) | [2665.06] | 0.92 | 2.07 | | 2.900(4) | | 149 | |
| N(4) --H(4A) ..F(9) | [ ] | 0.92 | 2.11 | | 2.885(4) | | 142 | |
| C(2) --H(2) ..F(16) | [2566.08] | 1.00 | 2.46 | | 3.367(5) | | 150 | |
| C(8) --H(8B) ..F(15) | [1556.08] | 0.99 | 2.43 | | 3.292(4) | | 145 | |
| C(17) --H(17) ..F(14) | [2665.08] | 1.00 | 2.48 | | 3.368(6) | | 148 | |
| C(27) --H(27) ..F(14) | [ ] | 1.00 | 2.21 | | 3.132(5) | | 152 | |
| C(29) --H(29) ..F(3) | [ ] | 1.00 | 2.25 | | 3.224(6) | | 163 | |

Translation of ARU-code to Equivalent Position Code

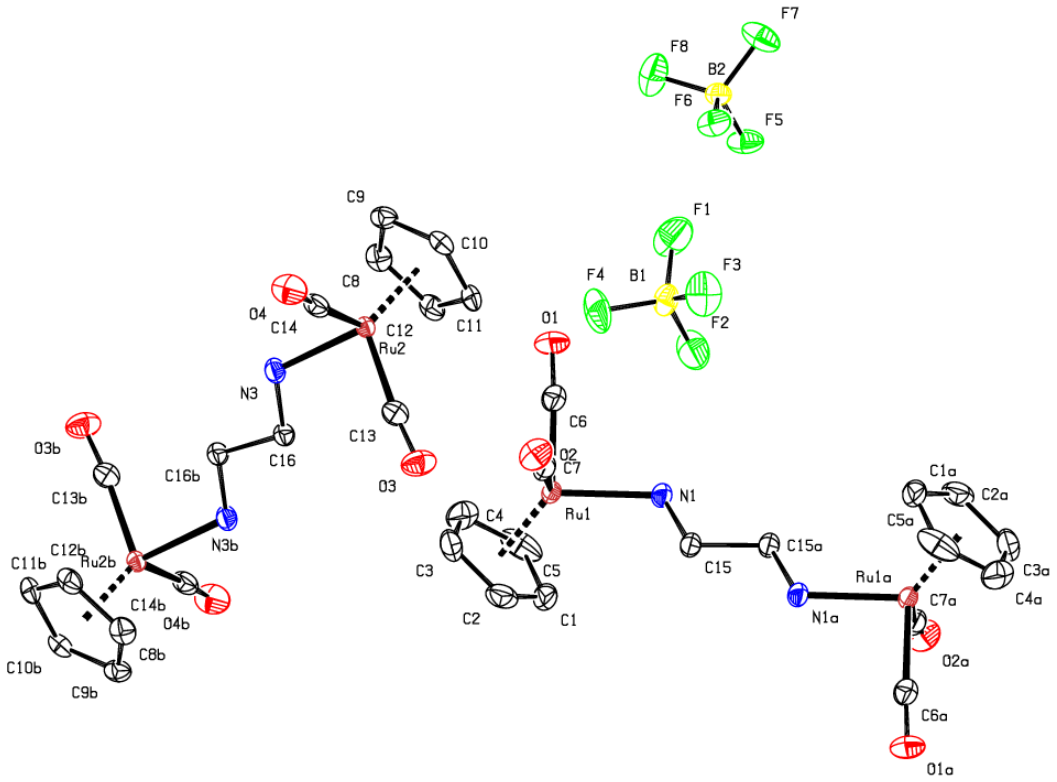
==========

[ 2666. ] = 1-x,1-y,1-z
[ 2566. ] = -x,1-y,1-z
[ 1556. ] = x,y,1+z

[ 2656. ] = 1-x,-y,1-z
[ 1655. ] = 1+x,y,z
[ 2756. ] = 2-x,-y,1-z
[ 2665. ] = 1-x,1-y,-z

For C--H...Acceptor Interactions See: Th. Steiner, Cryst. Rev, (1996), 6, 1-57

## Cyclopentadienyl ruthenium(II) 1,2-diethylamine complex – $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$ (Polymorph 2)




**ORTEP diagram**

**Table B54:** Crystal data and structure refinement for $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$.

| | | |
|---|---|---|
| Empirical formula | C16 H18 B2 F8 N2 O4 Ru2 | |
| Formula weight | 678.08 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P21/n | |
| Unit cell dimensions | a = 12.5336(5) Å | α= 90°. |
| | b = 12.9444(5) Å | β= 93.562(2)°. |
| | c = 13.7516(5) Å | γ = 90°. |
| Volume | 2226.75(15) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 2.023 $Mg/m^3$ | |
| Absorption coefficient | 1.450 $mm^{-1}$ | |
| F(000) | 1320 | |
| Crystal size | 0.37 x 0.19 x 0.14 $mm^3$ | |
| Theta range for data collection | 2.13 to 25.00°. | |
| Index ranges | -14<=h<=14, -15<=k<=14, -16<=l<=16 | |
| Reflections collected | 28701 | |
| Independent reflections | 3915 [R(int) = 0.0321] | |
| Completeness to theta = 25.00° | 99.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.8228 and 0.6161 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3915 / 0 / 307 | |
| Goodness-of-fit on $F^2$ | 1.026 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0238, wR2 = 0.0572 | |
| R indices (all data) | R1 = 0.0268, wR2 = 0.0595 | |
| Largest diff. peak and hole | 1.051 and -0.540 $e.Å^{-3}$ | |

**Table B55:** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $[\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 1615(3) | 40(3) | 55(3) | 38(1) |
| C(2) | 1540(3) | -511(3) | 913(3) | 35(1) |
| C(3) | 1056(3) | 120(3) | 1590(3) | 37(1) |
| C(4) | 815(3) | 1051(3) | 1153(3) | 39(1) |
| C(5) | 1161(3) | 1044(3) | 194(3) | 45(1) |
| C(6) | 2791(3) | 2258(3) | 1691(2) | 26(1) |
| C(7) | 3354(3) | 336(2) | 2357(2) | 24(1) |
| C(8) | 7532(3) | 2678(2) | 547(2) | 25(1) |
| C(9) | 8266(3) | 2719(2) | 1365(2) | 24(1) |
| C(10) | 9178(2) | 3284(2) | 1091(2) | 23(1) |
| C(11) | 8997(2) | 3572(2) | 96(2) | 25(1) |
| C(12) | 7968(3) | 3205(2) | -236(2) | 25(1) |
| C(13) | 8067(2) | 5642(3) | 408(2) | 24(1) |
| C(14) | 7951(3) | 4865(2) | 2255(2) | 26(1) |
| C(15) | 4519(2) | -60(2) | 308(2) | 22(1) |
| C(16) | 5608(2) | 5002(2) | -8(2) | 19(1) |
| N(1) | 3972(2) | 940(2) | 441(2) | 21(1) |
| N(3) | 6105(2) | 4588(2) | 907(2) | 23(1) |
| O(1) | 2863(2) | 3087(2) | 1950(2) | 37(1) |
| O(2) | 3762(2) | -11(2) | 3044(2) | 35(1) |
| O(3) | 8291(2) | 6384(2) | 30(2) | 37(1) |
| O(4) | 8084(2) | 5139(2) | 3036(2) | 39(1) |
| B(1) | 9427(3) | 7579(3) | 2353(3) | 30(1) |
| B(2) | 5038(3) | 7410(3) | 1421(3) | 24(1) |
| F(1) | 9327(2) | 8646(2) | 2237(2) | 64(1) |
| F(2) | 9656(2) | 7382(2) | 3324(2) | 64(1) |
| F(3) | 8445(2) | 7181(2) | 2047(2) | 56(1) |
| F(4) | 10219(2) | 7232(2) | 1789(2) | 55(1) |
| F(5) | 4788(2) | 7280(2) | 431(1) | 35(1) |
| F(6) | 5392(2) | 6478(1) | 1840(1) | 33(1) |
| F(7) | 5837(2) | 8147(2) | 1541(2) | 40(1) |
| F(8) | 4146(2) | 7738(2) | 1871(2) | 53(1) |
| Ru(1) | 2562(1) | 876(1) | 1250(1) | 17(1) |

| | | | | |
|---|---|---|---|---|
| Ru(2) | 7794(1) | 4335(1) | 962(1) | 15(1) |

**Table B56:** Bond lengths [Å] and angles [°] for $[\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$.

| | |
|---|---|
| C(1)-C(2) | 1.386(5) |
| C(1)-C(5) | 1.436(6) |
| C(1)-Ru(1) | 2.245(3) |
| C(1)-H(1) | 1.0000 |
| C(2)-C(3) | 1.406(5) |
| C(2)-Ru(1) | 2.237(3) |
| C(2)-H(2) | 1.0000 |
| C(3)-C(4) | 1.371(6) |
| C(3)-Ru(1) | 2.202(3) |
| C(3)-H(3) | 1.0000 |
| C(4)-C(5) | 1.415(6) |
| C(4)-Ru(1) | 2.197(3) |
| C(4)-H(4) | 1.0000 |
| C(5)-Ru(1) | 2.219(4) |
| C(5)-H(5) | 1.0000 |
| C(6)-O(1) | 1.132(4) |
| C(6)-Ru(1) | 1.905(3) |
| C(7)-O(2) | 1.138(4) |
| C(7)-Ru(1) | 1.899(3) |
| C(8)-C(9) | 1.409(5) |
| C(8)-C(12) | 1.413(5) |
| C(8)-Ru(2) | 2.239(3) |
| C(8)-H(8) | 1.0000 |
| C(9)-C(10) | 1.427(4) |
| C(9)-Ru(2) | 2.235(3) |
| C(9)-H(9) | 1.0000 |
| C(10)-C(11) | 1.423(4) |
| C(10)-Ru(2) | 2.203(3) |
| C(10)-H(10) | 1.0000 |
| C(11)-C(12) | 1.423(5) |
| C(11)-Ru(2) | 2.213(3) |

| | |
|---|---|
| C(11)-H(11) | 1.0000 |
| C(12)-Ru(2) | 2.224(3) |
| C(12)-H(12) | 1.0000 |
| C(13)-O(3) | 1.136(4) |
| C(13)-Ru(2) | 1.895(3) |
| C(14)-O(4) | 1.132(4) |
| C(14)-Ru(2) | 1.905(3) |
| C(15)-N(1) | 1.482(4) |
| C(15)-C(15)#1 | 1.524(6) |
| C(15)-H(15A) | 0.9900 |
| C(15)-H(15B) | 0.9900 |
| C(16)-N(3) | 1.471(4) |
| C(16)-C(16)#2 | 1.527(5) |
| C(16)-H(16A) | 0.9900 |
| C(16)-H(16B) | 0.9900 |
| N(1)-Ru(1) | 2.148(2) |
| N(1)-H(1A) | 0.9200 |
| N(1)-H(1B) | 0.9200 |
| N(3)-Ru(2) | 2.139(2) |
| N(3)-H(3A) | 0.9200 |
| N(3)-H(3B) | 0.9200 |
| B(1)-F(2) | 1.372(4) |
| B(1)-F(4) | 1.372(4) |
| B(1)-F(3) | 1.376(5) |
| B(1)-F(1) | 1.395(5) |
| B(2)-F(8) | 1.378(4) |
| B(2)-F(7) | 1.385(4) |
| B(2)-F(5) | 1.388(4) |
| B(2)-F(6) | 1.397(4) |

| | |
|---|---|
| C(2)-C(1)-C(5) | 107.7(3) |
| C(2)-C(1)-Ru(1) | 71.7(2) |
| C(5)-C(1)-Ru(1) | 70.2(2) |
| C(2)-C(1)-H(1) | 126.1 |
| C(5)-C(1)-H(1) | 126.1 |
| Ru(1)-C(1)-H(1) | 126.1 |
| C(1)-C(2)-C(3) | 108.6(3) |
| C(1)-C(2)-Ru(1) | 72.3(2) |

| | |
|---|---|
| C(3)-C(2)-Ru(1) | 70.2(2) |
| C(1)-C(2)-H(2) | 125.7 |
| C(3)-C(2)-H(2) | 125.7 |
| Ru(1)-C(2)-H(2) | 125.7 |
| C(4)-C(3)-C(2) | 108.2(3) |
| C(4)-C(3)-Ru(1) | 71.7(2) |
| C(2)-C(3)-Ru(1) | 72.9(2) |
| C(4)-C(3)-H(3) | 125.8 |
| C(2)-C(3)-H(3) | 125.8 |
| Ru(1)-C(3)-H(3) | 125.8 |
| C(3)-C(4)-C(5) | 109.3(3) |
| C(3)-C(4)-Ru(1) | 72.0(2) |
| C(5)-C(4)-Ru(1) | 72.1(2) |
| C(3)-C(4)-H(4) | 125.3 |
| C(5)-C(4)-H(4) | 125.3 |
| Ru(1)-C(4)-H(4) | 125.3 |
| C(4)-C(5)-C(1) | 106.1(3) |
| C(4)-C(5)-Ru(1) | 70.5(2) |
| C(1)-C(5)-Ru(1) | 72.2(2) |
| C(4)-C(5)-H(5) | 126.8 |
| C(1)-C(5)-H(5) | 126.8 |
| Ru(1)-C(5)-H(5) | 126.8 |
| O(1)-C(6)-Ru(1) | 175.9(3) |
| O(2)-C(7)-Ru(1) | 175.1(3) |
| C(9)-C(8)-C(12) | 109.0(3) |
| C(9)-C(8)-Ru(2) | 71.48(17) |
| C(12)-C(8)-Ru(2) | 70.98(17) |
| C(9)-C(8)-H(8) | 125.5 |
| C(12)-C(8)-H(8) | 125.5 |
| Ru(2)-C(8)-H(8) | 125.5 |
| C(8)-C(9)-C(10) | 107.6(3) |
| C(8)-C(9)-Ru(2) | 71.82(17) |
| C(10)-C(9)-Ru(2) | 70.03(17) |
| C(8)-C(9)-H(9) | 126.2 |
| C(10)-C(9)-H(9) | 126.2 |
| Ru(2)-C(9)-H(9) | 126.2 |
| C(11)-C(10)-C(9) | 107.8(3) |
| C(11)-C(10)-Ru(2) | 71.58(17) |

| | |
|---|---|
| C(9)-C(10)-Ru(2) | 72.46(17) |
| C(11)-C(10)-H(10) | 126.0 |
| C(9)-C(10)-H(10) | 126.0 |
| Ru(2)-C(10)-H(10) | 126.0 |
| C(12)-C(11)-C(10) | 107.9(3) |
| C(12)-C(11)-Ru(2) | 71.73(17) |
| C(10)-C(11)-Ru(2) | 70.81(17) |
| C(12)-C(11)-H(11) | 126.0 |
| C(10)-C(11)-H(11) | 126.0 |
| Ru(2)-C(11)-H(11) | 126.0 |
| C(8)-C(12)-C(11) | 107.6(3) |
| C(8)-C(12)-Ru(2) | 72.12(17) |
| C(11)-C(12)-Ru(2) | 70.85(17) |
| C(8)-C(12)-H(12) | 126.1 |
| C(11)-C(12)-H(12) | 126.1 |
| Ru(2)-C(12)-H(12) | 126.1 |
| O(3)-C(13)-Ru(2) | 174.2(3) |
| O(4)-C(14)-Ru(2) | 176.2(3) |
| N(1)-C(15)-C(15)#1 | 111.5(3) |
| N(1)-C(15)-H(15A) | 109.3 |
| C(15)#1-C(15)-H(15A) | 109.3 |
| N(1)-C(15)-H(15B) | 109.3 |
| C(15)#1-C(15)-H(15B) | 109.3 |
| H(15A)-C(15)-H(15B) | 108.0 |
| N(3)-C(16)-C(16)#2 | 110.8(3) |
| N(3)-C(16)-H(16A) | 109.5 |
| C(16)#2-C(16)-H(16A) | 109.5 |
| N(3)-C(16)-H(16B) | 109.5 |
| C(16)#2-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16B) | 108.1 |
| C(15)-N(1)-Ru(1) | 115.58(18) |
| C(15)-N(1)-H(1A) | 108.4 |
| Ru(1)-N(1)-H(1A) | 108.4 |
| C(15)-N(1)-H(1B) | 108.4 |
| Ru(1)-N(1)-H(1B) | 108.4 |
| H(1A)-N(1)-H(1B) | 107.4 |
| C(16)-N(3)-Ru(2) | 116.83(18) |
| C(16)-N(3)-H(3A) | 108.1 |

| | |
|---|---|
| Ru(2)-N(3)-H(3A) | 108.1 |
| C(16)-N(3)-H(3B) | 108.1 |
| Ru(2)-N(3)-H(3B) | 108.1 |
| H(3A)-N(3)-H(3B) | 107.3 |
| F(2)-B(1)-F(4) | 112.0(3) |
| F(2)-B(1)-F(3) | 110.9(3) |
| F(4)-B(1)-F(3) | 111.7(3) |
| F(2)-B(1)-F(1) | 107.9(3) |
| F(4)-B(1)-F(1) | 108.9(3) |
| F(3)-B(1)-F(1) | 105.3(3) |
| F(8)-B(2)-F(7) | 109.6(3) |
| F(8)-B(2)-F(5) | 109.7(3) |
| F(7)-B(2)-F(5) | 108.5(3) |
| F(8)-B(2)-F(6) | 109.1(3) |
| F(7)-B(2)-F(6) | 109.8(3) |
| F(5)-B(2)-F(6) | 110.2(3) |
| C(7)-Ru(1)-C(6) | 91.68(14) |
| C(7)-Ru(1)-N(1) | 91.34(11) |
| C(6)-Ru(1)-N(1) | 90.91(12) |
| C(7)-Ru(1)-C(4) | 123.79(15) |
| C(6)-Ru(1)-C(4) | 92.99(14) |
| N(1)-Ru(1)-C(4) | 144.47(13) |
| C(7)-Ru(1)-C(3) | 94.52(14) |
| C(6)-Ru(1)-C(3) | 117.62(14) |
| N(1)-Ru(1)-C(3) | 150.61(12) |
| C(4)-Ru(1)-C(3) | 36.33(15) |
| C(7)-Ru(1)-C(5) | 156.11(14) |
| C(6)-Ru(1)-C(5) | 102.34(14) |
| N(1)-Ru(1)-C(5) | 107.48(14) |
| C(4)-Ru(1)-C(5) | 37.36(16) |
| C(3)-Ru(1)-C(5) | 61.88(15) |
| C(7)-Ru(1)-C(2) | 97.77(14) |
| C(6)-Ru(1)-C(2) | 153.21(13) |
| N(1)-Ru(1)-C(2) | 113.75(12) |
| C(4)-Ru(1)-C(2) | 60.97(14) |
| C(3)-Ru(1)-C(2) | 36.90(14) |
| C(5)-Ru(1)-C(2) | 61.54(14) |
| C(7)-Ru(1)-C(1) | 129.50(15) |

| | |
|---|---|
| C(6)-Ru(1)-C(1) | 138.43(15) |
| N(1)-Ru(1)-C(1) | 93.13(11) |
| C(4)-Ru(1)-C(1) | 61.68(13) |
| C(3)-Ru(1)-C(1) | 61.30(13) |
| C(5)-Ru(1)-C(1) | 37.53(15) |
| C(2)-Ru(1)-C(1) | 36.03(14) |
| C(13)-Ru(2)-C(14) | 92.46(14) |
| C(13)-Ru(2)-N(3) | 93.02(12) |
| C(14)-Ru(2)-N(3) | 91.29(12) |
| C(13)-Ru(2)-C(10) | 115.01(13) |
| C(14)-Ru(2)-C(10) | 96.45(12) |
| N(3)-Ru(2)-C(10) | 150.43(11) |
| C(13)-Ru(2)-C(11) | 92.07(13) |
| C(14)-Ru(2)-C(11) | 129.02(13) |
| N(3)-Ru(2)-C(11) | 139.07(11) |
| C(10)-Ru(2)-C(11) | 37.61(12) |
| C(13)-Ru(2)-C(12) | 105.15(13) |
| C(14)-Ru(2)-C(12) | 156.81(12) |
| N(3)-Ru(2)-C(12) | 102.50(11) |
| C(10)-Ru(2)-C(12) | 62.64(12) |
| C(11)-Ru(2)-C(12) | 37.42(12) |
| C(13)-Ru(2)-C(9) | 152.10(13) |
| C(14)-Ru(2)-C(9) | 95.48(12) |
| N(3)-Ru(2)-C(9) | 113.45(11) |
| C(10)-Ru(2)-C(9) | 37.51(12) |
| C(11)-Ru(2)-C(9) | 62.38(12) |
| C(12)-Ru(2)-C(9) | 62.02(12) |
| C(13)-Ru(2)-C(8) | 141.28(13) |
| C(14)-Ru(2)-C(8) | 126.02(13) |
| N(3)-Ru(2)-C(8) | 90.47(11) |
| C(10)-Ru(2)-C(8) | 62.02(12) |
| C(11)-Ru(2)-C(8) | 61.87(12) |
| C(12)-Ru(2)-C(8) | 36.90(12) |
| C(9)-Ru(2)-C(8) | 36.71(12) |

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Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z  #2 -x+1,-y+1,-z

**Table B57:** Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 28(2) | 58(3) | 30(2) | -19(2) | 9(2) | -13(2) |
| C(2) | 34(2) | 20(2) | 50(2) | -6(2) | 1(2) | -4(1) |
| C(3) | 26(2) | 50(2) | 36(2) | -2(2) | 11(2) | -13(2) |
| C(4) | 21(2) | 44(2) | 52(2) | -19(2) | -3(2) | 10(2) |
| C(5) | 44(2) | 38(2) | 48(2) | 18(2) | -26(2) | -16(2) |
| C(6) | 26(2) | 29(2) | 22(2) | 0(1) | 4(1) | 1(1) |
| C(7) | 27(2) | 24(2) | 23(2) | -1(1) | 9(1) | 2(1) |
| C(8) | 28(2) | 18(2) | 30(2) | -8(1) | 3(1) | -2(1) |
| C(9) | 30(2) | 16(2) | 25(2) | -1(1) | 1(1) | 2(1) |
| C(10) | 20(2) | 22(2) | 28(2) | -2(1) | -1(1) | 8(1) |
| C(11) | 23(2) | 25(2) | 28(2) | -2(1) | 9(1) | 7(1) |
| C(12) | 29(2) | 24(2) | 20(2) | -8(1) | 1(1) | 8(1) |
| C(13) | 22(2) | 25(2) | 26(2) | -2(1) | -4(1) | 1(1) |
| C(14) | 29(2) | 21(2) | 28(2) | -2(1) | 2(1) | 9(1) |
| C(15) | 22(2) | 21(2) | 23(2) | -1(1) | 7(1) | 1(1) |
| C(16) | 16(2) | 20(2) | 21(2) | 0(1) | 2(1) | 1(1) |
| N(1) | 23(1) | 21(1) | 19(1) | 1(1) | 7(1) | -1(1) |
| N(3) | 17(1) | 30(2) | 20(1) | 1(1) | 2(1) | 4(1) |
| O(1) | 48(2) | 21(1) | 42(2) | -9(1) | 1(1) | -1(1) |
| O(2) | 45(2) | 37(1) | 24(1) | 4(1) | -1(1) | 6(1) |
| O(3) | 40(1) | 27(1) | 42(2) | 9(1) | -3(1) | -7(1) |
| O(4) | 59(2) | 38(2) | 19(1) | -8(1) | -3(1) | 12(1) |
| B(1) | 36(2) | 31(2) | 24(2) | -8(2) | 10(2) | -4(2) |
| B(2) | 28(2) | 21(2) | 22(2) | -2(1) | 0(1) | -3(1) |
| F(1) | 101(2) | 39(1) | 56(2) | -4(1) | 32(2) | -6(1) |
| F(2) | 57(2) | 108(2) | 26(1) | 7(1) | 4(1) | 37(2) |
| F(3) | 48(1) | 62(2) | 57(2) | -16(1) | 4(1) | -12(1) |
| F(4) | 46(1) | 84(2) | 34(1) | -19(1) | 11(1) | 20(1) |
| F(5) | 54(1) | 26(1) | 23(1) | -1(1) | -7(1) | -5(1) |
| F(6) | 50(1) | 24(1) | 24(1) | 2(1) | 0(1) | 1(1) |
| F(7) | 47(1) | 37(1) | 34(1) | 11(1) | -15(1) | -19(1) |
| F(8) | 48(1) | 59(2) | 53(1) | 5(1) | 22(1) | 14(1) |
| Ru(1) | 19(1) | 16(1) | 17(1) | 0(1) | 5(1) | 1(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Ru(2) | 15(1) | 17(1) | 15(1) | -1(1) | 1(1) | 2(1) |

**Table B58:** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 1896 | -228 | -561 | 46 |
| H(2) | 1762 | -1247 | 1020 | 42 |
| H(3) | 856 | -96 | 2253 | 45 |
| H(4) | 413 | 1626 | 1450 | 47 |
| H(5) | 1044 | 1597 | -309 | 53 |
| H(8) | 6829 | 2311 | 518 | 30 |
| H(9) | 8181 | 2379 | 2009 | 28 |
| H(10) | 9851 | 3398 | 1505 | 28 |
| H(11) | 9520 | 3927 | -311 | 30 |
| H(12) | 7637 | 3261 | -914 | 30 |
| H(15A) | 4009 | -556 | -13 | 26 |
| H(15B) | 4757 | -345 | 953 | 26 |
| H(16A) | 5827 | 4579 | -562 | 23 |
| H(16B) | 5861 | 5718 | -104 | 23 |
| H(1A) | 3789 | 1213 | -164 | 25 |
| H(1B) | 4450 | 1388 | 753 | 25 |
| H(3A) | 5779 | 3969 | 1034 | 27 |
| H(3B) | 5960 | 5035 | 1402 | 27 |

**Table B59:** Torsion angles [°] for $\{[\eta^5\text{-}C_5H_5Ru(CO)_2]_2NH_2(CH_2)_2NH_2\}(BF_4)_2$.

| | |
|---|---|
| C(5)-C(1)-C(2)-C(3) | -0.2(4) |
| Ru(1)-C(1)-C(2)-C(3) | 61.1(2) |
| C(5)-C(1)-C(2)-Ru(1) | -61.3(2) |
| C(1)-C(2)-C(3)-C(4) | 1.0(4) |
| Ru(1)-C(2)-C(3)-C(4) | 63.4(3) |
| C(1)-C(2)-C(3)-Ru(1) | -62.4(3) |
| C(2)-C(3)-C(4)-C(5) | -1.3(4) |
| Ru(1)-C(3)-C(4)-C(5) | 62.9(3) |
| C(2)-C(3)-C(4)-Ru(1) | -64.2(2) |
| C(3)-C(4)-C(5)-C(1) | 1.1(4) |
| Ru(1)-C(4)-C(5)-C(1) | 64.0(2) |
| C(3)-C(4)-C(5)-Ru(1) | -62.8(3) |
| C(2)-C(1)-C(5)-C(4) | -0.5(4) |
| Ru(1)-C(1)-C(5)-C(4) | -62.8(2) |
| C(2)-C(1)-C(5)-Ru(1) | 62.3(3) |
| C(12)-C(8)-C(9)-C(10) | 0.1(3) |
| Ru(2)-C(8)-C(9)-C(10) | -61.2(2) |
| C(12)-C(8)-C(9)-Ru(2) | 61.4(2) |
| C(8)-C(9)-C(10)-C(11) | -0.9(3) |
| Ru(2)-C(9)-C(10)-C(11) | -63.3(2) |
| C(8)-C(9)-C(10)-Ru(2) | 62.4(2) |
| C(9)-C(10)-C(11)-C(12) | 1.3(3) |
| Ru(2)-C(10)-C(11)-C(12) | -62.5(2) |
| C(9)-C(10)-C(11)-Ru(2) | 63.9(2) |
| C(9)-C(8)-C(12)-C(11) | 0.7(3) |
| Ru(2)-C(8)-C(12)-C(11) | 62.3(2) |
| C(9)-C(8)-C(12)-Ru(2) | -61.7(2) |
| C(10)-C(11)-C(12)-C(8) | -1.2(3) |
| Ru(2)-C(11)-C(12)-C(8) | -63.2(2) |
| C(10)-C(11)-C(12)-Ru(2) | 61.9(2) |
| C(15)#1-C(15)-N(1)-Ru(1) | 177.7(3) |
| C(16)#2-C(16)-N(3)-Ru(2) | 172.0(2) |
| O(2)-C(7)-Ru(1)-C(6) | 108(3) |
| O(2)-C(7)-Ru(1)-N(1) | -161(3) |
| O(2)-C(7)-Ru(1)-C(4) | 14(3) |
| O(2)-C(7)-Ru(1)-C(3) | -9(3) |

| | |
|---|---|
| O(2)-C(7)-Ru(1)-C(5) | -18(4) |
| O(2)-C(7)-Ru(1)-C(2) | -46(3) |
| O(2)-C(7)-Ru(1)-C(1) | -66(3) |
| O(1)-C(6)-Ru(1)-C(7) | -124(4) |
| O(1)-C(6)-Ru(1)-N(1) | 145(4) |
| O(1)-C(6)-Ru(1)-C(4) | 0(4) |
| O(1)-C(6)-Ru(1)-C(3) | -28(4) |
| O(1)-C(6)-Ru(1)-C(5) | 37(4) |
| O(1)-C(6)-Ru(1)-C(2) | -13(4) |
| O(1)-C(6)-Ru(1)-C(1) | 49(4) |
| C(15)-N(1)-Ru(1)-C(7) | 59.7(2) |
| C(15)-N(1)-Ru(1)-C(6) | 151.4(2) |
| C(15)-N(1)-Ru(1)-C(4) | -112.2(3) |
| C(15)-N(1)-Ru(1)-C(3) | -42.0(4) |
| C(15)-N(1)-Ru(1)-C(5) | -105.4(2) |
| C(15)-N(1)-Ru(1)-C(2) | -39.4(2) |
| C(15)-N(1)-Ru(1)-C(1) | -70.0(2) |
| C(3)-C(4)-Ru(1)-C(7) | -41.4(3) |
| C(5)-C(4)-Ru(1)-C(7) | -159.4(2) |
| C(3)-C(4)-Ru(1)-C(6) | -135.4(2) |
| C(5)-C(4)-Ru(1)-C(6) | 106.5(2) |
| C(3)-C(4)-Ru(1)-N(1) | 128.8(2) |
| C(5)-C(4)-Ru(1)-N(1) | 10.8(3) |
| C(5)-C(4)-Ru(1)-C(3) | -118.0(3) |
| C(3)-C(4)-Ru(1)-C(5) | 118.0(3) |
| C(3)-C(4)-Ru(1)-C(2) | 37.9(2) |
| C(5)-C(4)-Ru(1)-C(2) | -80.1(2) |
| C(3)-C(4)-Ru(1)-C(1) | 79.2(2) |
| C(5)-C(4)-Ru(1)-C(1) | -38.9(2) |
| C(4)-C(3)-Ru(1)-C(7) | 146.5(2) |
| C(2)-C(3)-Ru(1)-C(7) | -96.9(2) |
| C(4)-C(3)-Ru(1)-C(6) | 52.3(3) |
| C(2)-C(3)-Ru(1)-C(6) | 168.8(2) |
| C(4)-C(3)-Ru(1)-N(1) | -112.6(3) |
| C(2)-C(3)-Ru(1)-N(1) | 3.9(4) |
| C(2)-C(3)-Ru(1)-C(4) | 116.5(3) |
| C(4)-C(3)-Ru(1)-C(5) | -37.4(2) |
| C(2)-C(3)-Ru(1)-C(5) | 79.2(3) |

| | |
|---|---|
| C(4)-C(3)-Ru(1)-C(2) | -116.5(3) |
| C(4)-C(3)-Ru(1)-C(1) | -80.3(2) |
| C(2)-C(3)-Ru(1)-C(1) | 36.3(2) |
| C(4)-C(5)-Ru(1)-C(7) | 46.1(5) |
| C(1)-C(5)-Ru(1)-C(7) | -68.9(5) |
| C(4)-C(5)-Ru(1)-C(6) | -78.5(2) |
| C(1)-C(5)-Ru(1)-C(6) | 166.5(2) |
| C(4)-C(5)-Ru(1)-N(1) | -173.5(2) |
| C(1)-C(5)-Ru(1)-N(1) | 71.6(2) |
| C(1)-C(5)-Ru(1)-C(4) | -114.9(3) |
| C(4)-C(5)-Ru(1)-C(3) | 36.4(2) |
| C(1)-C(5)-Ru(1)-C(3) | -78.6(2) |
| C(4)-C(5)-Ru(1)-C(2) | 78.5(2) |
| C(1)-C(5)-Ru(1)-C(2) | -36.5(2) |
| C(4)-C(5)-Ru(1)-C(1) | 114.9(3) |
| C(1)-C(2)-Ru(1)-C(7) | -154.7(2) |
| C(3)-C(2)-Ru(1)-C(7) | 87.2(2) |
| C(1)-C(2)-Ru(1)-C(6) | 95.7(4) |
| C(3)-C(2)-Ru(1)-C(6) | -22.4(4) |
| C(1)-C(2)-Ru(1)-N(1) | -59.8(2) |
| C(3)-C(2)-Ru(1)-N(1) | -177.9(2) |
| C(1)-C(2)-Ru(1)-C(4) | 80.8(2) |
| C(3)-C(2)-Ru(1)-C(4) | -37.3(2) |
| C(1)-C(2)-Ru(1)-C(3) | 118.1(3) |
| C(1)-C(2)-Ru(1)-C(5) | 38.0(2) |
| C(3)-C(2)-Ru(1)-C(5) | -80.2(3) |
| C(3)-C(2)-Ru(1)-C(1) | -118.1(3) |
| C(2)-C(1)-Ru(1)-C(7) | 33.3(3) |
| C(5)-C(1)-Ru(1)-C(7) | 150.7(2) |
| C(2)-C(1)-Ru(1)-C(6) | -137.5(2) |
| C(5)-C(1)-Ru(1)-C(6) | -20.1(3) |
| C(2)-C(1)-Ru(1)-N(1) | 127.6(2) |
| C(5)-C(1)-Ru(1)-N(1) | -115.0(2) |
| C(2)-C(1)-Ru(1)-C(4) | -78.7(2) |
| C(5)-C(1)-Ru(1)-C(4) | 38.7(2) |
| C(2)-C(1)-Ru(1)-C(3) | -37.1(2) |
| C(5)-C(1)-Ru(1)-C(3) | 80.2(2) |
| C(2)-C(1)-Ru(1)-C(5) | -117.4(3) |

| | |
|---|---|
| C(5)-C(1)-Ru(1)-C(2) | 117.4(3) |
| O(3)-C(13)-Ru(2)-C(14) | 131(3) |
| O(3)-C(13)-Ru(2)-N(3) | -138(3) |
| O(3)-C(13)-Ru(2)-C(10) | 33(3) |
| O(3)-C(13)-Ru(2)-C(11) | 2(3) |
| O(3)-C(13)-Ru(2)-C(12) | -34(3) |
| O(3)-C(13)-Ru(2)-C(9) | 24(3) |
| O(3)-C(13)-Ru(2)-C(8) | -43(3) |
| O(4)-C(14)-Ru(2)-C(13) | -126(5) |
| O(4)-C(14)-Ru(2)-N(3) | 141(5) |
| O(4)-C(14)-Ru(2)-C(10) | -11(5) |
| O(4)-C(14)-Ru(2)-C(11) | -32(5) |
| O(4)-C(14)-Ru(2)-C(12) | 14(5) |
| O(4)-C(14)-Ru(2)-C(9) | 27(5) |
| O(4)-C(14)-Ru(2)-C(8) | 49(5) |
| C(16)-N(3)-Ru(2)-C(13) | 46.2(2) |
| C(16)-N(3)-Ru(2)-C(14) | 138.8(2) |
| C(16)-N(3)-Ru(2)-C(10) | -115.7(3) |
| C(16)-N(3)-Ru(2)-C(11) | -50.4(3) |
| C(16)-N(3)-Ru(2)-C(12) | -60.0(2) |
| C(16)-N(3)-Ru(2)-C(9) | -124.7(2) |
| C(16)-N(3)-Ru(2)-C(8) | -95.2(2) |
| C(11)-C(10)-Ru(2)-C(13) | -57.3(2) |
| C(9)-C(10)-Ru(2)-C(13) | -173.63(18) |
| C(11)-C(10)-Ru(2)-C(14) | -153.1(2) |
| C(9)-C(10)-Ru(2)-C(14) | 90.6(2) |
| C(11)-C(10)-Ru(2)-N(3) | 102.7(3) |
| C(9)-C(10)-Ru(2)-N(3) | -13.6(3) |
| C(9)-C(10)-Ru(2)-C(11) | -116.3(3) |
| C(11)-C(10)-Ru(2)-C(12) | 37.47(19) |
| C(9)-C(10)-Ru(2)-C(12) | -78.9(2) |
| C(11)-C(10)-Ru(2)-C(9) | 116.3(3) |
| C(11)-C(10)-Ru(2)-C(8) | 79.3(2) |
| C(9)-C(10)-Ru(2)-C(8) | -36.99(18) |
| C(12)-C(11)-Ru(2)-C(13) | -112.5(2) |
| C(10)-C(11)-Ru(2)-C(13) | 130.3(2) |
| C(12)-C(11)-Ru(2)-C(14) | 152.6(2) |
| C(10)-C(11)-Ru(2)-C(14) | 35.4(3) |

| | |
|---|---|
| C(12)-C(11)-Ru(2)-N(3) | -15.5(3) |
| C(10)-C(11)-Ru(2)-N(3) | -132.7(2) |
| C(12)-C(11)-Ru(2)-C(10) | 117.2(3) |
| C(10)-C(11)-Ru(2)-C(12) | -117.2(3) |
| C(12)-C(11)-Ru(2)-C(9) | 79.2(2) |
| C(10)-C(11)-Ru(2)-C(9) | -38.02(18) |
| C(12)-C(11)-Ru(2)-C(8) | 37.47(19) |
| C(10)-C(11)-Ru(2)-C(8) | -79.8(2) |
| C(8)-C(12)-Ru(2)-C(13) | -170.32(19) |
| C(11)-C(12)-Ru(2)-C(13) | 73.0(2) |
| C(8)-C(12)-Ru(2)-C(14) | 51.5(4) |
| C(11)-C(12)-Ru(2)-C(14) | -65.2(4) |
| C(8)-C(12)-Ru(2)-N(3) | -73.67(19) |
| C(11)-C(12)-Ru(2)-N(3) | 169.67(18) |
| C(8)-C(12)-Ru(2)-C(10) | 79.0(2) |
| C(11)-C(12)-Ru(2)-C(10) | -37.66(18) |
| C(8)-C(12)-Ru(2)-C(11) | 116.7(3) |
| C(8)-C(12)-Ru(2)-C(9) | 36.44(19) |
| C(11)-C(12)-Ru(2)-C(9) | -80.2(2) |
| C(11)-C(12)-Ru(2)-C(8) | -116.7(3) |
| C(8)-C(9)-Ru(2)-C(13) | -104.9(3) |
| C(10)-C(9)-Ru(2)-C(13) | 12.4(4) |
| C(8)-C(9)-Ru(2)-C(14) | 149.3(2) |
| C(10)-C(9)-Ru(2)-C(14) | -93.5(2) |
| C(8)-C(9)-Ru(2)-N(3) | 55.5(2) |
| C(10)-C(9)-Ru(2)-N(3) | 172.75(17) |
| C(8)-C(9)-Ru(2)-C(10) | -117.3(3) |
| C(8)-C(9)-Ru(2)-C(11) | -79.1(2) |
| C(10)-C(9)-Ru(2)-C(11) | 38.12(18) |
| C(8)-C(9)-Ru(2)-C(12) | -36.63(19) |
| C(10)-C(9)-Ru(2)-C(12) | 80.6(2) |
| C(10)-C(9)-Ru(2)-C(8) | 117.3(3) |
| C(9)-C(8)-Ru(2)-C(13) | 133.7(2) |
| C(12)-C(8)-Ru(2)-C(13) | 15.0(3) |
| C(9)-C(8)-Ru(2)-C(14) | -39.0(2) |
| C(12)-C(8)-Ru(2)-C(14) | -157.61(19) |
| C(9)-C(8)-Ru(2)-N(3) | -130.90(19) |
| C(12)-C(8)-Ru(2)-N(3) | 110.45(19) |

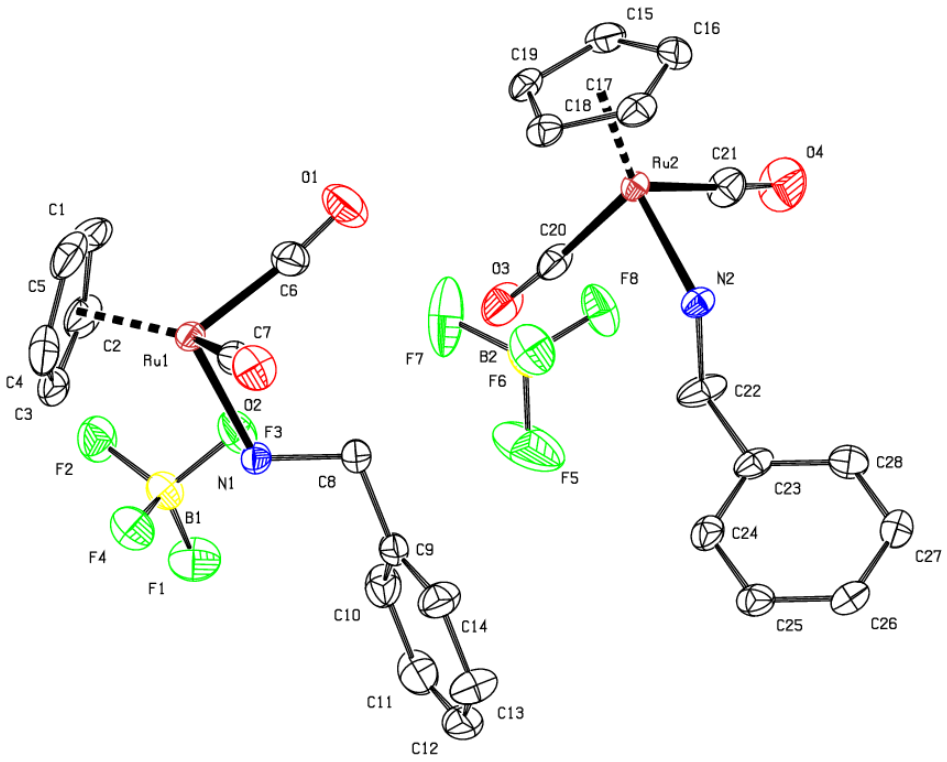
| | |
|---|---|
| C(9)-C(8)-Ru(2)-C(10) | 37.80(19) |
| C(12)-C(8)-Ru(2)-C(10) | -80.9(2) |
| C(9)-C(8)-Ru(2)-C(11) | 80.6(2) |
| C(12)-C(8)-Ru(2)-C(11) | -38.00(18) |
| C(9)-C(8)-Ru(2)-C(12) | 118.6(3) |
| C(12)-C(8)-Ru(2)-C(9) | -118.6(3) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z  #2 -x+1,-y+1,-z

# STRUCTURE TABLES PERTAINING TO CHAPTER 6

## Cyclopentadienyl ruthenium(II) benzylamine complex - $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2C_6H_5]BF_4$.




**ORTEP diagram**

**Table B60:** Crystal data and structure refinement for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2C_6H_5]BF_4$.

| | | |
|---|---|---|
| Empirical formula | C14 H14 B F4 N O2 Ru | |
| Formula weight | 416.14 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P21/n | |
| Unit cell dimensions | a = 10.4488(3) Å | α= 90°. |
| | b = 9.7788(4) Å | β= 99.2360(10)°. |
| | c = 31.7901(11) Å | γ = 90°. |
| Volume | 3206.10(19) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.724 $Mg/m^3$ | |
| Absorption coefficient | 1.025 $mm^{-1}$ | |
| F(000) | 1648 | |
| Crystal size | 0.39 x 0.28 x 0.14 $mm^3$ | |
| Theta range for data collection | 1.98 to 28.45°. | |
| Index ranges | -13<=h<=14, -11<=k<=13, -42<=l<=42 | |
| Reflections collected | 40725 | |
| Independent reflections | 8054 [R(int) = 0.0185] | |
| Completeness to theta = 28.45° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.8698 and 0.6907 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 8054 / 0 / 415 | |
| Goodness-of-fit on $F^2$ | 1.090 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0238, wR2 = 0.0546 | |
| R indices (all data) | R1 = 0.0259, wR2 = 0.0557 | |
| Largest diff. peak and hole | 0.827 and -0.479 $e.Å^{-3}$ | |

**Table B61:** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2C_6H_5]BF_4$.. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 5946(3) | 4080(3) | 2972(1) | 48(1) |
| C(2) | 4674(2) | 3648(3) | 3014(1) | 38(1) |
| C(3) | 4676(2) | 2205(3) | 3007(1) | 34(1) |
| C(4) | 5913(2) | 1741(3) | 2959(1) | 40(1) |
| C(5) | 6710(2) | 2918(3) | 2932(1) | 47(1) |
| C(6) | 5252(2) | 4538(2) | 2045(1) | 31(1) |
| C(7) | 5917(2) | 1848(2) | 2013(1) | 26(1) |
| C(8) | 2715(2) | 3084(2) | 1652(1) | 27(1) |
| C(9) | 1447(2) | 2472(2) | 1444(1) | 26(1) |
| C(10) | 286(2) | 2826(3) | 1579(1) | 35(1) |
| C(11) | -875(2) | 2243(3) | 1385(1) | 44(1) |
| C(12) | -885(2) | 1313(3) | 1060(1) | 44(1) |
| C(13) | 255(2) | 963(3) | 925(1) | 46(1) |
| C(14) | 1422(2) | 1544(3) | 1117(1) | 36(1) |
| C(15) | 5487(2) | 9168(2) | 947(1) | 30(1) |
| C(16) | 5745(2) | 8708(2) | 541(1) | 32(1) |
| C(17) | 5986(2) | 7291(2) | 571(1) | 28(1) |
| C(18) | 5888(2) | 6849(2) | 989(1) | 25(1) |
| C(19) | 5587(2) | 8024(2) | 1222(1) | 26(1) |
| C(20) | 2867(2) | 7098(2) | 1078(1) | 28(1) |
| C(21) | 2749(2) | 8935(2) | 415(1) | 32(1) |
| C(22) | 1879(2) | 5657(3) | 220(1) | 36(1) |
| C(23) | 1477(2) | 4647(2) | -134(1) | 26(1) |
| C(24) | 1406(2) | 3262(2) | -48(1) | 27(1) |
| C(25) | 1034(2) | 2337(2) | -375(1) | 28(1) |
| C(26) | 741(2) | 2786(2) | -791(1) | 27(1) |
| C(27) | 810(2) | 4165(2) | -880(1) | 28(1) |
| C(28) | 1177(2) | 5094(2) | -553(1) | 28(1) |
| N(1) | 3229(1) | 2416(2) | 2065(1) | 22(1) |
| N(2) | 3230(1) | 6136(2) | 240(1) | 21(1) |
| O(1) | 5424(2) | 5509(2) | 1868(1) | 49(1) |
| O(2) | 6463(2) | 1155(2) | 1818(1) | 38(1) |
| O(3) | 2268(2) | 6747(2) | 1326(1) | 45(1) |

| | | | | |
|---|---|---|---|---|
| O(4) | 2056(2) | 9722(2) | 244(1) | 53(1) |
| B(1) | 973(2) | 3786(3) | 2754(1) | 29(1) |
| B(2) | 5292(2) | 2862(3) | 684(1) | 31(1) |
| F(1) | -364(1) | 3719(2) | 2647(1) | 45(1) |
| F(2) | 1301(1) | 4414(2) | 3150(1) | 41(1) |
| F(3) | 1491(1) | 4570(1) | 2454(1) | 37(1) |
| F(4) | 1506(1) | 2483(1) | 2759(1) | 38(1) |
| F(5) | 4165(2) | 2133(2) | 629(1) | 87(1) |
| F(6) | 6247(1) | 2107(1) | 530(1) | 43(1) |
| F(7) | 5686(2) | 3176(2) | 1101(1) | 79(1) |
| F(8) | 5117(1) | 4054(1) | 439(1) | 40(1) |
| Ru(1) | 5125(1) | 2969(1) | 2385(1) | 21(1) |
| Ru(2) | 3968(1) | 7671(1) | 694(1) | 18(1) |

**Table B62:** Bond lengths [Å] and angles [°] for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2C_6H_5]BF_4$.

| | |
|---|---|
| C(1)-C(5) | 1.406(4) |
| C(1)-C(2) | 1.422(3) |
| C(1)-Ru(1) | 2.210(2) |
| C(1)-H(1) | 1.0000 |
| C(2)-C(3) | 1.411(4) |
| C(2)-Ru(1) | 2.227(2) |
| C(2)-H(2) | 1.0000 |
| C(3)-C(4) | 1.401(3) |
| C(3)-Ru(1) | 2.233(2) |
| C(3)-H(3) | 1.0000 |
| C(4)-C(5) | 1.432(4) |
| C(4)-Ru(1) | 2.230(2) |
| C(4)-H(4) | 1.0000 |
| C(5)-Ru(1) | 2.201(2) |
| C(5)-H(5) | 1.0000 |
| C(6)-O(1) | 1.133(3) |
| C(6)-Ru(1) | 1.894(2) |
| C(7)-O(2) | 1.132(3) |
| C(7)-Ru(1) | 1.898(2) |
| C(8)-N(1) | 1.487(2) |
| C(8)-C(9) | 1.506(3) |
| C(8)-H(8A) | 0.9900 |
| C(8)-H(8B) | 0.9900 |
| C(9)-C(14) | 1.377(3) |
| C(9)-C(10) | 1.393(3) |
| C(10)-C(11) | 1.391(3) |
| C(10)-H(10) | 0.9500 |
| C(11)-C(12) | 1.374(4) |
| C(11)-H(11) | 0.9500 |
| C(12)-C(13) | 1.374(4) |
| C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.393(3) |
| C(13)-H(13) | 0.9500 |
| C(14)-H(14) | 0.9500 |
| C(15)-C(19) | 1.412(3) |
| C(15)-C(16) | 1.433(3) |

| | |
|---|---|
| C(15)-Ru(2) | 2.2132(19) |
| C(15)-H(15) | 1.0000 |
| C(16)-C(17) | 1.408(3) |
| C(16)-Ru(2) | 2.2361(19) |
| C(16)-H(16) | 1.0000 |
| C(17)-C(18) | 1.418(3) |
| C(17)-Ru(2) | 2.2360(18) |
| C(17)-H(17) | 1.0000 |
| C(18)-C(19) | 1.428(3) |
| C(18)-Ru(2) | 2.2247(18) |
| C(18)-H(18) | 1.0000 |
| C(19)-Ru(2) | 2.2101(18) |
| C(19)-H(19) | 1.0000 |
| C(20)-O(3) | 1.136(3) |
| C(20)-Ru(2) | 1.893(2) |
| C(21)-O(4) | 1.134(3) |
| C(21)-Ru(2) | 1.890(2) |
| C(22)-N(2) | 1.479(2) |
| C(22)-C(23) | 1.505(3) |
| C(22)-H(22A) | 0.9900 |
| C(22)-H(22B) | 0.9900 |
| C(23)-C(24) | 1.386(3) |
| C(23)-C(28) | 1.389(3) |
| C(24)-C(25) | 1.387(3) |
| C(24)-H(24) | 0.9500 |
| C(25)-C(26) | 1.381(3) |
| C(25)-H(25) | 0.9500 |
| C(26)-C(27) | 1.382(3) |
| C(26)-H(26) | 0.9500 |
| C(27)-C(28) | 1.388(3) |
| C(27)-H(27) | 0.9500 |
| C(28)-H(28) | 0.9500 |
| N(1)-Ru(1) | 2.1464(15) |
| N(1)-H(1A) | 0.9200 |
| N(1)-H(1B) | 0.9200 |
| N(2)-Ru(2) | 2.1378(15) |
| N(2)-H(2A) | 0.9200 |
| N(2)-H(2B) | 0.9200 |

| | |
|---|---|
| B(1)-F(1) | 1.386(3) |
| B(1)-F(4) | 1.390(3) |
| B(1)-F(2) | 1.393(3) |
| B(1)-F(3) | 1.399(3) |
| B(2)-F(7) | 1.359(3) |
| B(2)-F(5) | 1.364(3) |
| B(2)-F(6) | 1.392(3) |
| B(2)-F(8) | 1.397(3) |

| | |
|---|---|
| C(5)-C(1)-C(2) | 108.7(2) |
| C(5)-C(1)-Ru(1) | 71.06(13) |
| C(2)-C(1)-Ru(1) | 71.98(12) |
| C(5)-C(1)-H(1) | 125.6 |
| C(2)-C(1)-H(1) | 125.6 |
| Ru(1)-C(1)-H(1) | 125.6 |
| C(3)-C(2)-C(1) | 107.0(2) |
| C(3)-C(2)-Ru(1) | 71.80(12) |
| C(1)-C(2)-Ru(1) | 70.64(12) |
| C(3)-C(2)-H(2) | 126.4 |
| C(1)-C(2)-H(2) | 126.4 |
| Ru(1)-C(2)-H(2) | 126.4 |
| C(4)-C(3)-C(2) | 109.3(2) |
| C(4)-C(3)-Ru(1) | 71.56(12) |
| C(2)-C(3)-Ru(1) | 71.32(12) |
| C(4)-C(3)-H(3) | 125.3 |
| C(2)-C(3)-H(3) | 125.3 |
| Ru(1)-C(3)-H(3) | 125.3 |
| C(3)-C(4)-C(5) | 107.6(2) |
| C(3)-C(4)-Ru(1) | 71.85(13) |
| C(5)-C(4)-Ru(1) | 70.04(13) |
| C(3)-C(4)-H(4) | 126.2 |
| C(5)-C(4)-H(4) | 126.2 |
| Ru(1)-C(4)-H(4) | 126.2 |
| C(1)-C(5)-C(4) | 107.4(2) |
| C(1)-C(5)-Ru(1) | 71.75(13) |
| C(4)-C(5)-Ru(1) | 72.24(12) |
| C(1)-C(5)-H(5) | 126.1 |
| C(4)-C(5)-H(5) | 126.1 |

| | |
|---|---|
| Ru(1)-C(5)-H(5) | 126.1 |
| O(1)-C(6)-Ru(1) | 173.7(2) |
| O(2)-C(7)-Ru(1) | 174.46(18) |
| N(1)-C(8)-C(9) | 112.34(16) |
| N(1)-C(8)-H(8A) | 109.1 |
| C(9)-C(8)-H(8A) | 109.1 |
| N(1)-C(8)-H(8B) | 109.1 |
| C(9)-C(8)-H(8B) | 109.1 |
| H(8A)-C(8)-H(8B) | 107.9 |
| C(14)-C(9)-C(10) | 118.91(19) |
| C(14)-C(9)-C(8) | 120.09(19) |
| C(10)-C(9)-C(8) | 121.0(2) |
| C(11)-C(10)-C(9) | 120.1(2) |
| C(11)-C(10)-H(10) | 119.9 |
| C(9)-C(10)-H(10) | 119.9 |
| C(12)-C(11)-C(10) | 120.4(2) |
| C(12)-C(11)-H(11) | 119.8 |
| C(10)-C(11)-H(11) | 119.8 |
| C(13)-C(12)-C(11) | 119.8(2) |
| C(13)-C(12)-H(12) | 120.1 |
| C(11)-C(12)-H(12) | 120.1 |
| C(12)-C(13)-C(14) | 120.2(2) |
| C(12)-C(13)-H(13) | 119.9 |
| C(14)-C(13)-H(13) | 119.9 |
| C(9)-C(14)-C(13) | 120.6(2) |
| C(9)-C(14)-H(14) | 119.7 |
| C(13)-C(14)-H(14) | 119.7 |
| C(19)-C(15)-C(16) | 107.56(19) |
| C(19)-C(15)-Ru(2) | 71.26(11) |
| C(16)-C(15)-Ru(2) | 72.08(11) |
| C(19)-C(15)-H(15) | 126.1 |
| C(16)-C(15)-H(15) | 126.1 |
| Ru(2)-C(15)-H(15) | 126.1 |
| C(17)-C(16)-C(15) | 107.80(18) |
| C(17)-C(16)-Ru(2) | 71.64(11) |
| C(15)-C(16)-Ru(2) | 70.35(11) |
| C(17)-C(16)-H(16) | 126.1 |
| C(15)-C(16)-H(16) | 126.1 |

| | |
|---|---|
| Ru(2)-C(16)-H(16) | 126.1 |
| C(16)-C(17)-C(18) | 108.94(18) |
| C(16)-C(17)-Ru(2) | 71.65(11) |
| C(18)-C(17)-Ru(2) | 71.03(10) |
| C(16)-C(17)-H(17) | 125.5 |
| C(18)-C(17)-H(17) | 125.5 |
| Ru(2)-C(17)-H(17) | 125.5 |
| C(17)-C(18)-C(19) | 107.10(18) |
| C(17)-C(18)-Ru(2) | 71.90(11) |
| C(19)-C(18)-Ru(2) | 70.66(10) |
| C(17)-C(18)-H(18) | 126.4 |
| C(19)-C(18)-H(18) | 126.4 |
| Ru(2)-C(18)-H(18) | 126.4 |
| C(15)-C(19)-C(18) | 108.59(18) |
| C(15)-C(19)-Ru(2) | 71.50(11) |
| C(18)-C(19)-Ru(2) | 71.76(10) |
| C(15)-C(19)-H(19) | 125.7 |
| C(18)-C(19)-H(19) | 125.7 |
| Ru(2)-C(19)-H(19) | 125.7 |
| O(3)-C(20)-Ru(2) | 176.03(18) |
| O(4)-C(21)-Ru(2) | 177.4(2) |
| N(2)-C(22)-C(23) | 113.00(16) |
| N(2)-C(22)-H(22A) | 109.0 |
| C(23)-C(22)-H(22A) | 109.0 |
| N(2)-C(22)-H(22B) | 109.0 |
| C(23)-C(22)-H(22B) | 109.0 |
| H(22A)-C(22)-H(22B) | 107.8 |
| C(24)-C(23)-C(28) | 119.06(18) |
| C(24)-C(23)-C(22) | 120.7(2) |
| C(28)-C(23)-C(22) | 120.2(2) |
| C(23)-C(24)-C(25) | 120.43(19) |
| C(23)-C(24)-H(24) | 119.8 |
| C(25)-C(24)-H(24) | 119.8 |
| C(26)-C(25)-C(24) | 120.2(2) |
| C(26)-C(25)-H(25) | 119.9 |
| C(24)-C(25)-H(25) | 119.9 |
| C(25)-C(26)-C(27) | 119.74(19) |
| C(25)-C(26)-H(26) | 120.1 |

| | |
|---|---|
| C(27)-C(26)-H(26) | 120.1 |
| C(26)-C(27)-C(28) | 120.11(19) |
| C(26)-C(27)-H(27) | 119.9 |
| C(28)-C(27)-H(27) | 119.9 |
| C(27)-C(28)-C(23) | 120.4(2) |
| C(27)-C(28)-H(28) | 119.8 |
| C(23)-C(28)-H(28) | 119.8 |
| C(8)-N(1)-Ru(1) | 118.89(12) |
| C(8)-N(1)-H(1A) | 107.6 |
| Ru(1)-N(1)-H(1A) | 107.6 |
| C(8)-N(1)-H(1B) | 107.6 |
| Ru(1)-N(1)-H(1B) | 107.6 |
| H(1A)-N(1)-H(1B) | 107.0 |
| C(22)-N(2)-Ru(2) | 119.41(12) |
| C(22)-N(2)-H(2A) | 107.5 |
| Ru(2)-N(2)-H(2A) | 107.5 |
| C(22)-N(2)-H(2B) | 107.5 |
| Ru(2)-N(2)-H(2B) | 107.5 |
| H(2A)-N(2)-H(2B) | 107.0 |
| F(1)-B(1)-F(4) | 110.19(19) |
| F(1)-B(1)-F(2) | 109.55(18) |
| F(4)-B(1)-F(2) | 110.83(19) |
| F(1)-B(1)-F(3) | 110.07(19) |
| F(4)-B(1)-F(3) | 108.13(17) |
| F(2)-B(1)-F(3) | 108.03(19) |
| F(7)-B(2)-F(5) | 111.2(2) |
| F(7)-B(2)-F(6) | 109.9(2) |
| F(5)-B(2)-F(6) | 109.3(2) |
| F(7)-B(2)-F(8) | 110.3(2) |
| F(5)-B(2)-F(8) | 109.4(2) |
| F(6)-B(2)-F(8) | 106.54(17) |
| C(6)-Ru(1)-C(7) | 91.96(9) |
| C(6)-Ru(1)-N(1) | 94.41(8) |
| C(7)-Ru(1)-N(1) | 91.13(7) |
| C(6)-Ru(1)-C(5) | 110.90(10) |
| C(7)-Ru(1)-C(5) | 97.55(10) |
| N(1)-Ru(1)-C(5) | 152.81(8) |
| C(6)-Ru(1)-C(1) | 91.76(10) |

| | |
|---|---|
| C(7)-Ru(1)-C(1) | 131.42(10) |
| N(1)-Ru(1)-C(1) | 136.75(9) |
| C(5)-Ru(1)-C(1) | 37.19(11) |
| C(6)-Ru(1)-C(2) | 108.40(10) |
| C(7)-Ru(1)-C(2) | 155.25(9) |
| N(1)-Ru(1)-C(2) | 100.88(7) |
| C(5)-Ru(1)-C(2) | 62.54(9) |
| C(1)-Ru(1)-C(2) | 37.38(9) |
| C(6)-Ru(1)-C(4) | 148.61(10) |
| C(7)-Ru(1)-C(4) | 93.37(9) |
| N(1)-Ru(1)-C(4) | 116.37(8) |
| C(5)-Ru(1)-C(4) | 37.72(10) |
| C(1)-Ru(1)-C(4) | 62.06(11) |
| C(2)-Ru(1)-C(4) | 61.92(9) |
| C(6)-Ru(1)-C(3) | 145.16(9) |
| C(7)-Ru(1)-C(3) | 122.25(9) |
| N(1)-Ru(1)-C(3) | 91.54(7) |
| C(5)-Ru(1)-C(3) | 62.06(8) |
| C(1)-Ru(1)-C(3) | 61.65(9) |
| C(2)-Ru(1)-C(3) | 36.88(9) |
| C(4)-Ru(1)-C(3) | 36.59(8) |
| C(21)-Ru(2)-C(20) | 93.60(9) |
| C(21)-Ru(2)-N(2) | 89.96(8) |
| C(20)-Ru(2)-N(2) | 92.06(7) |
| C(21)-Ru(2)-C(19) | 129.08(9) |
| C(20)-Ru(2)-C(19) | 91.54(8) |
| N(2)-Ru(2)-C(19) | 140.44(7) |
| C(21)-Ru(2)-C(15) | 97.38(9) |
| C(20)-Ru(2)-C(15) | 115.84(8) |
| N(2)-Ru(2)-C(15) | 150.45(7) |
| C(19)-Ru(2)-C(15) | 37.24(8) |
| C(21)-Ru(2)-C(18) | 158.23(9) |
| C(20)-Ru(2)-C(18) | 102.74(8) |
| N(2)-Ru(2)-C(18) | 103.54(7) |
| C(19)-Ru(2)-C(18) | 37.58(7) |
| C(15)-Ru(2)-C(18) | 62.63(8) |
| C(21)-Ru(2)-C(17) | 127.59(9) |
| C(20)-Ru(2)-C(17) | 138.71(9) |

| | |
|---|---|
| N(2)-Ru(2)-C(17) | 90.81(7) |
| C(19)-Ru(2)-C(17) | 61.98(7) |
| C(15)-Ru(2)-C(17) | 62.12(8) |
| C(18)-Ru(2)-C(17) | 37.07(7) |
| C(21)-Ru(2)-C(16) | 97.04(9) |
| C(20)-Ru(2)-C(16) | 152.44(8) |
| N(2)-Ru(2)-C(16) | 113.24(7) |
| C(19)-Ru(2)-C(16) | 62.16(8) |
| C(15)-Ru(2)-C(16) | 37.57(8) |
| C(18)-Ru(2)-C(16) | 62.08(8) |
| C(17)-Ru(2)-C(16) | 36.71(8) |

**Table B63:** Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2C_6H_5]BF_4$. The anisotropicdisplacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 56(2) | 62(2) | 25(1) | -14(1) | 4(1) | -31(1) |
| C(2) | 39(1) | 54(2) | 20(1) | -12(1) | 7(1) | -4(1) |
| C(3) | 32(1) | 53(1) | 17(1) | 1(1) | 6(1) | -9(1) |
| C(4) | 38(1) | 60(2) | 22(1) | 9(1) | 2(1) | 7(1) |
| C(5) | 24(1) | 94(2) | 22(1) | -1(1) | -1(1) | -11(1) |
| C(6) | 32(1) | 32(1) | 30(1) | -2(1) | 8(1) | -6(1) |
| C(7) | 20(1) | 34(1) | 26(1) | 2(1) | 5(1) | -3(1) |
| C(8) | 26(1) | 32(1) | 21(1) | 5(1) | 1(1) | -5(1) |
| C(9) | 23(1) | 31(1) | 24(1) | 9(1) | -1(1) | -4(1) |
| C(10) | 28(1) | 44(1) | 32(1) | 7(1) | 3(1) | 4(1) |
| C(11) | 22(1) | 58(2) | 49(1) | 22(1) | 3(1) | 2(1) |
| C(12) | 29(1) | 48(2) | 51(1) | 18(1) | -11(1) | -14(1) |
| C(13) | 41(1) | 47(2) | 47(1) | -7(1) | -5(1) | -15(1) |
| C(14) | 27(1) | 44(1) | 36(1) | -6(1) | 2(1) | -7(1) |
| C(15) | 26(1) | 24(1) | 37(1) | -3(1) | -3(1) | -5(1) |
| C(16) | 23(1) | 41(1) | 31(1) | 9(1) | 2(1) | -10(1) |
| C(17) | 15(1) | 41(1) | 30(1) | -7(1) | 7(1) | -3(1) |
| C(18) | 15(1) | 27(1) | 31(1) | 0(1) | -1(1) | 2(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(19) | 19(1) | 33(1) | 23(1) | -3(1) | -2(1) | -2(1) |
| C(20) | 19(1) | 43(1) | 22(1) | -7(1) | 1(1) | -2(1) |
| C(21) | 30(1) | 30(1) | 33(1) | -3(1) | 0(1) | 5(1) |
| C(22) | 20(1) | 52(1) | 39(1) | -24(1) | 11(1) | -12(1) |
| C(23) | 15(1) | 37(1) | 26(1) | -11(1) | 6(1) | -4(1) |
| C(24) | 17(1) | 41(1) | 24(1) | 1(1) | 1(1) | -2(1) |
| C(25) | 20(1) | 26(1) | 36(1) | 1(1) | -1(1) | -1(1) |
| C(26) | 21(1) | 30(1) | 29(1) | -8(1) | -1(1) | 0(1) |
| C(27) | 28(1) | 33(1) | 23(1) | 0(1) | 2(1) | 2(1) |
| C(28) | 26(1) | 24(1) | 34(1) | -2(1) | 7(1) | -1(1) |
| N(1) | 18(1) | 27(1) | 20(1) | 2(1) | 3(1) | -1(1) |
| N(2) | 15(1) | 27(1) | 21(1) | -5(1) | 4(1) | -1(1) |
| O(1) | 68(1) | 34(1) | 48(1) | 7(1) | 19(1) | -10(1) |
| O(2) | 34(1) | 44(1) | 40(1) | -1(1) | 17(1) | 5(1) |
| O(3) | 32(1) | 81(1) | 25(1) | -8(1) | 11(1) | -16(1) |
| O(4) | 50(1) | 42(1) | 62(1) | 8(1) | -10(1) | 20(1) |
| B(1) | 28(1) | 30(1) | 30(1) | 1(1) | 11(1) | 2(1) |
| B(2) | 29(1) | 33(1) | 33(1) | 13(1) | 10(1) | 5(1) |
| F(1) | 26(1) | 51(1) | 60(1) | -2(1) | 12(1) | 2(1) |
| F(2) | 53(1) | 42(1) | 29(1) | -2(1) | 11(1) | 0(1) |
| F(3) | 46(1) | 37(1) | 33(1) | 4(1) | 18(1) | 0(1) |
| F(4) | 40(1) | 31(1) | 46(1) | 4(1) | 12(1) | 6(1) |
| F(5) | 36(1) | 76(1) | 150(2) | 43(1) | 21(1) | -8(1) |
| F(6) | 42(1) | 37(1) | 52(1) | 10(1) | 15(1) | 15(1) |
| F(7) | 100(2) | 111(2) | 24(1) | 11(1) | 11(1) | 36(1) |
| F(8) | 61(1) | 29(1) | 36(1) | 10(1) | 20(1) | 14(1) |
| Ru(1) | 17(1) | 28(1) | 18(1) | -1(1) | 4(1) | -4(1) |
| Ru(2) | 15(1) | 20(1) | 17(1) | -1(1) | 2(1) | 1(1) |

**Table B64:** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for [$\eta^5$-$C_5H_5Ru(CO)_2NH_2CH_2C_6H_5]BF_4$.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 6260 | 5048 | 2986 | 57 |
| H(2) | 3938 | 4250 | 3063 | 45 |
| H(3) | 3925 | 1609 | 3044 | 40 |
| H(4) | 6200 | 765 | 2961 | 48 |
| H(5) | 7659 | 2913 | 2917 | 57 |
| H(8A) | 3360 | 2991 | 1456 | 32 |
| H(8B) | 2591 | 4072 | 1700 | 32 |
| H(10) | 287 | 3467 | 1803 | 42 |
| H(11) | -1664 | 2488 | 1478 | 52 |
| H(12) | -1679 | 914 | 930 | 53 |
| H(13) | 249 | 324 | 700 | 56 |
| H(14) | 2207 | 1296 | 1022 | 43 |
| H(15) | 5340 | 10137 | 1028 | 36 |
| H(16) | 5795 | 9296 | 287 | 38 |
| H(17) | 6227 | 6702 | 339 | 34 |
| H(18) | 6067 | 5906 | 1106 | 30 |
| H(19) | 5517 | 8045 | 1532 | 31 |
| H(22A) | 1289 | 6455 | 179 | 43 |
| H(22B) | 1785 | 5225 | 495 | 43 |
| H(24) | 1613 | 2944 | 237 | 33 |
| H(25) | 982 | 1390 | -313 | 33 |
| H(26) | 492 | 2151 | -1015 | 32 |
| H(27) | 607 | 4478 | -1166 | 34 |
| H(28) | 1223 | 6041 | -616 | 34 |
| H(1A) | 3227 | 1487 | 2019 | 26 |
| H(1B) | 2652 | 2585 | 2249 | 26 |
| H(2A) | 3314 | 6460 | -25 | 25 |
| H(2B) | 3762 | 5385 | 291 | 25 |

**Table B65:** Torsion angles [°] for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2C_6H_5]BF_4$.

| | |
|---|---|
| C(5)-C(1)-C(2)-C(3) | 1.1(3) |
| Ru(1)-C(1)-C(2)-C(3) | 63.03(15) |
| C(5)-C(1)-C(2)-Ru(1) | -61.92(16) |
| C(1)-C(2)-C(3)-C(4) | -0.4(2) |
| Ru(1)-C(2)-C(3)-C(4) | 61.86(15) |
| C(1)-C(2)-C(3)-Ru(1) | -62.27(15) |
| C(2)-C(3)-C(4)-C(5) | -0.4(2) |
| Ru(1)-C(3)-C(4)-C(5) | 61.28(15) |
| C(2)-C(3)-C(4)-Ru(1) | -61.71(15) |
| C(2)-C(1)-C(5)-C(4) | -1.4(3) |
| Ru(1)-C(1)-C(5)-C(4) | -63.88(15) |
| C(2)-C(1)-C(5)-Ru(1) | 62.50(16) |
| C(3)-C(4)-C(5)-C(1) | 1.1(2) |
| Ru(1)-C(4)-C(5)-C(1) | 63.56(16) |
| C(3)-C(4)-C(5)-Ru(1) | -62.45(15) |
| N(1)-C(8)-C(9)-C(14) | -100.6(2) |
| N(1)-C(8)-C(9)-C(10) | 79.1(2) |
| C(14)-C(9)-C(10)-C(11) | 0.2(3) |
| C(8)-C(9)-C(10)-C(11) | -179.5(2) |
| C(9)-C(10)-C(11)-C(12) | 0.1(4) |
| C(10)-C(11)-C(12)-C(13) | -0.3(4) |
| C(11)-C(12)-C(13)-C(14) | 0.3(4) |
| C(10)-C(9)-C(14)-C(13) | -0.2(3) |
| C(8)-C(9)-C(14)-C(13) | 179.5(2) |
| C(12)-C(13)-C(14)-C(9) | 0.0(4) |
| C(19)-C(15)-C(16)-C(17) | 0.6(2) |
| Ru(2)-C(15)-C(16)-C(17) | -62.23(13) |
| C(19)-C(15)-C(16)-Ru(2) | 62.84(13) |
| C(15)-C(16)-C(17)-C(18) | -0.2(2) |
| Ru(2)-C(16)-C(17)-C(18) | -61.58(13) |
| C(15)-C(16)-C(17)-Ru(2) | 61.41(14) |
| C(16)-C(17)-C(18)-C(19) | -0.3(2) |
| Ru(2)-C(17)-C(18)-C(19) | -62.28(12) |
| C(16)-C(17)-C(18)-Ru(2) | 61.97(13) |
| C(16)-C(15)-C(19)-C(18) | -0.8(2) |
| Ru(2)-C(15)-C(19)-C(18) | 62.57(13) |

| | |
|---|---|
| C(16)-C(15)-C(19)-Ru(2) | -63.37(13) |
| C(17)-C(18)-C(19)-C(15) | 0.7(2) |
| Ru(2)-C(18)-C(19)-C(15) | -62.40(13) |
| C(17)-C(18)-C(19)-Ru(2) | 63.10(13) |
| N(2)-C(22)-C(23)-C(24) | 103.3(2) |
| N(2)-C(22)-C(23)-C(28) | -76.4(3) |
| C(28)-C(23)-C(24)-C(25) | -0.3(3) |
| C(22)-C(23)-C(24)-C(25) | 179.99(17) |
| C(23)-C(24)-C(25)-C(26) | 0.5(3) |
| C(24)-C(25)-C(26)-C(27) | -0.4(3) |
| C(25)-C(26)-C(27)-C(28) | 0.2(3) |
| C(26)-C(27)-C(28)-C(23) | 0.0(3) |
| C(24)-C(23)-C(28)-C(27) | 0.1(3) |
| C(22)-C(23)-C(28)-C(27) | 179.77(18) |
| C(9)-C(8)-N(1)-Ru(1) | 173.43(13) |
| C(23)-C(22)-N(2)-Ru(2) | 176.12(15) |
| O(1)-C(6)-Ru(1)-C(7) | -100.7(19) |
| O(1)-C(6)-Ru(1)-N(1) | 168.0(19) |
| O(1)-C(6)-Ru(1)-C(5) | -1.9(19) |
| O(1)-C(6)-Ru(1)-C(1) | 30.8(19) |
| O(1)-C(6)-Ru(1)-C(2) | 65.0(19) |
| O(1)-C(6)-Ru(1)-C(4) | -1(2) |
| O(1)-C(6)-Ru(1)-C(3) | 68.9(19) |
| O(2)-C(7)-Ru(1)-C(6) | 122.0(19) |
| O(2)-C(7)-Ru(1)-N(1) | -143.6(19) |
| O(2)-C(7)-Ru(1)-C(5) | 10.6(19) |
| O(2)-C(7)-Ru(1)-C(1) | 28(2) |
| O(2)-C(7)-Ru(1)-C(2) | -24(2) |
| O(2)-C(7)-Ru(1)-C(4) | -27.1(19) |
| O(2)-C(7)-Ru(1)-C(3) | -51.1(19) |
| C(8)-N(1)-Ru(1)-C(6) | 13.59(15) |
| C(8)-N(1)-Ru(1)-C(7) | -78.46(15) |
| C(8)-N(1)-Ru(1)-C(5) | 172.5(2) |
| C(8)-N(1)-Ru(1)-C(1) | 110.88(17) |
| C(8)-N(1)-Ru(1)-C(2) | 123.29(15) |
| C(8)-N(1)-Ru(1)-C(4) | -172.79(14) |
| C(8)-N(1)-Ru(1)-C(3) | 159.23(15) |
| C(1)-C(5)-Ru(1)-C(6) | 63.33(16) |

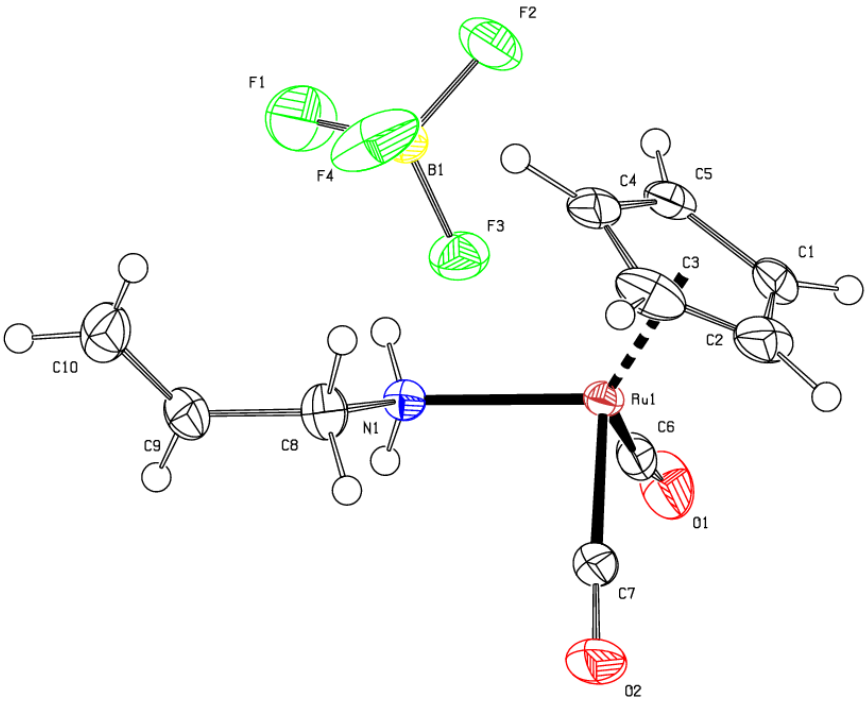
| | |
|---|---|
| C(4)-C(5)-Ru(1)-C(6) | 179.25(14) |
| C(1)-C(5)-Ru(1)-C(7) | 158.35(15) |
| C(4)-C(5)-Ru(1)-C(7) | -85.73(15) |
| C(1)-C(5)-Ru(1)-N(1) | -94.1(2) |
| C(4)-C(5)-Ru(1)-N(1) | 21.8(3) |
| C(4)-C(5)-Ru(1)-C(1) | 115.9(2) |
| C(1)-C(5)-Ru(1)-C(2) | -37.18(14) |
| C(4)-C(5)-Ru(1)-C(2) | 78.74(15) |
| C(1)-C(5)-Ru(1)-C(4) | -115.9(2) |
| C(1)-C(5)-Ru(1)-C(3) | -79.04(15) |
| C(4)-C(5)-Ru(1)-C(3) | 36.88(14) |
| C(5)-C(1)-Ru(1)-C(6) | -123.36(15) |
| C(2)-C(1)-Ru(1)-C(6) | 118.68(17) |
| C(5)-C(1)-Ru(1)-C(7) | -29.2(2) |
| C(2)-C(1)-Ru(1)-C(7) | -147.15(16) |
| C(5)-C(1)-Ru(1)-N(1) | 138.30(14) |
| C(2)-C(1)-Ru(1)-N(1) | 20.3(2) |
| C(2)-C(1)-Ru(1)-C(5) | -118.0(2) |
| C(5)-C(1)-Ru(1)-C(2) | 118.0(2) |
| C(5)-C(1)-Ru(1)-C(4) | 38.53(14) |
| C(2)-C(1)-Ru(1)-C(4) | -79.43(17) |
| C(5)-C(1)-Ru(1)-C(3) | 80.23(16) |
| C(2)-C(1)-Ru(1)-C(3) | -37.72(15) |
| C(3)-C(2)-Ru(1)-C(6) | 176.27(13) |
| C(1)-C(2)-Ru(1)-C(6) | -67.54(18) |
| C(3)-C(2)-Ru(1)-C(7) | -39.9(3) |
| C(1)-C(2)-Ru(1)-C(7) | 76.3(3) |
| C(3)-C(2)-Ru(1)-N(1) | 77.84(14) |
| C(1)-C(2)-Ru(1)-N(1) | -165.96(17) |
| C(3)-C(2)-Ru(1)-C(5) | -79.21(16) |
| C(1)-C(2)-Ru(1)-C(5) | 36.99(17) |
| C(3)-C(2)-Ru(1)-C(1) | -116.2(2) |
| C(3)-C(2)-Ru(1)-C(4) | -36.36(13) |
| C(1)-C(2)-Ru(1)-C(4) | 79.84(18) |
| C(1)-C(2)-Ru(1)-C(3) | 116.2(2) |
| C(3)-C(4)-Ru(1)-C(6) | 115.84(19) |
| C(5)-C(4)-Ru(1)-C(6) | -1.3(3) |
| C(3)-C(4)-Ru(1)-C(7) | -144.83(15) |

| | |
|---|---|
| C(5)-C(4)-Ru(1)-C(7) | 97.99(16) |
| C(3)-C(4)-Ru(1)-N(1) | -51.89(17) |
| C(5)-C(4)-Ru(1)-N(1) | -169.07(14) |
| C(3)-C(4)-Ru(1)-C(5) | 117.2(2) |
| C(3)-C(4)-Ru(1)-C(1) | 79.21(16) |
| C(5)-C(4)-Ru(1)-C(1) | -37.98(15) |
| C(3)-C(4)-Ru(1)-C(2) | 36.65(14) |
| C(5)-C(4)-Ru(1)-C(2) | -80.54(16) |
| C(5)-C(4)-Ru(1)-C(3) | -117.2(2) |
| C(4)-C(3)-Ru(1)-C(6) | -124.87(19) |
| C(2)-C(3)-Ru(1)-C(6) | -6.2(2) |
| C(4)-C(3)-Ru(1)-C(7) | 42.84(18) |
| C(2)-C(3)-Ru(1)-C(7) | 161.50(13) |
| C(4)-C(3)-Ru(1)-N(1) | 135.15(15) |
| C(2)-C(3)-Ru(1)-N(1) | -106.19(13) |
| C(4)-C(3)-Ru(1)-C(5) | -38.02(16) |
| C(2)-C(3)-Ru(1)-C(5) | 80.63(16) |
| C(4)-C(3)-Ru(1)-C(1) | -80.42(17) |
| C(2)-C(3)-Ru(1)-C(1) | 38.24(15) |
| C(4)-C(3)-Ru(1)-C(2) | -118.7(2) |
| C(2)-C(3)-Ru(1)-C(4) | 118.7(2) |
| O(4)-C(21)-Ru(2)-C(20) | 150(5) |
| O(4)-C(21)-Ru(2)-N(2) | -118(5) |
| O(4)-C(21)-Ru(2)-C(19) | 55(5) |
| O(4)-C(21)-Ru(2)-C(15) | 34(5) |
| O(4)-C(21)-Ru(2)-C(18) | 11(5) |
| O(4)-C(21)-Ru(2)-C(17) | -27(5) |
| O(4)-C(21)-Ru(2)-C(16) | -4(5) |
| O(3)-C(20)-Ru(2)-C(21) | -144(3) |
| O(3)-C(20)-Ru(2)-N(2) | 126(3) |
| O(3)-C(20)-Ru(2)-C(19) | -14(3) |
| O(3)-C(20)-Ru(2)-C(15) | -44(3) |
| O(3)-C(20)-Ru(2)-C(18) | 22(3) |
| O(3)-C(20)-Ru(2)-C(17) | 33(3) |
| O(3)-C(20)-Ru(2)-C(16) | -31(3) |
| C(22)-N(2)-Ru(2)-C(21) | -64.17(17) |
| C(22)-N(2)-Ru(2)-C(20) | 29.44(17) |
| C(22)-N(2)-Ru(2)-C(19) | 124.35(17) |

| | |
|---|---|
| C(22)-N(2)-Ru(2)-C(15) | -169.19(17) |
| C(22)-N(2)-Ru(2)-C(18) | 133.07(16) |
| C(22)-N(2)-Ru(2)-C(17) | 168.24(17) |
| C(22)-N(2)-Ru(2)-C(16) | -161.81(16) |
| C(15)-C(19)-Ru(2)-C(21) | -37.36(17) |
| C(18)-C(19)-Ru(2)-C(21) | -155.01(13) |
| C(15)-C(19)-Ru(2)-C(20) | -133.26(14) |
| C(18)-C(19)-Ru(2)-C(20) | 109.09(13) |
| C(15)-C(19)-Ru(2)-N(2) | 131.65(13) |
| C(18)-C(19)-Ru(2)-N(2) | 13.99(17) |
| C(18)-C(19)-Ru(2)-C(15) | -117.66(17) |
| C(15)-C(19)-Ru(2)-C(18) | 117.66(17) |
| C(15)-C(19)-Ru(2)-C(17) | 79.90(13) |
| C(18)-C(19)-Ru(2)-C(17) | -37.75(12) |
| C(15)-C(19)-Ru(2)-C(16) | 38.14(13) |
| C(18)-C(19)-Ru(2)-C(16) | -79.51(13) |
| C(19)-C(15)-Ru(2)-C(21) | 151.64(13) |
| C(16)-C(15)-Ru(2)-C(21) | -91.96(14) |
| C(19)-C(15)-Ru(2)-C(20) | 53.99(15) |
| C(16)-C(15)-Ru(2)-C(20) | 170.39(13) |
| C(19)-C(15)-Ru(2)-N(2) | -105.23(17) |
| C(16)-C(15)-Ru(2)-N(2) | 11.2(2) |
| C(16)-C(15)-Ru(2)-C(19) | 116.40(18) |
| C(19)-C(15)-Ru(2)-C(18) | -37.46(12) |
| C(16)-C(15)-Ru(2)-C(18) | 78.93(13) |
| C(19)-C(15)-Ru(2)-C(17) | -79.51(13) |
| C(16)-C(15)-Ru(2)-C(17) | 36.89(12) |
| C(19)-C(15)-Ru(2)-C(16) | -116.40(18) |
| C(17)-C(18)-Ru(2)-C(21) | -54.1(3) |
| C(19)-C(18)-Ru(2)-C(21) | 62.2(3) |
| C(17)-C(18)-Ru(2)-C(20) | 168.14(13) |
| C(19)-C(18)-Ru(2)-C(20) | -75.59(13) |
| C(17)-C(18)-Ru(2)-N(2) | 72.85(13) |
| C(19)-C(18)-Ru(2)-N(2) | -170.89(11) |
| C(17)-C(18)-Ru(2)-C(19) | -116.27(17) |
| C(17)-C(18)-Ru(2)-C(15) | -79.14(13) |
| C(19)-C(18)-Ru(2)-C(15) | 37.12(12) |
| C(19)-C(18)-Ru(2)-C(17) | 116.27(17) |

| | |
|---|---|
| C(17)-C(18)-Ru(2)-C(16) | -36.52(12) |
| C(19)-C(18)-Ru(2)-C(16) | 79.75(13) |
| C(16)-C(17)-Ru(2)-C(21) | 39.32(16) |
| C(18)-C(17)-Ru(2)-C(21) | 157.72(13) |
| C(16)-C(17)-Ru(2)-C(20) | -136.08(14) |
| C(18)-C(17)-Ru(2)-C(20) | -17.68(18) |
| C(16)-C(17)-Ru(2)-N(2) | 129.88(13) |
| C(18)-C(17)-Ru(2)-N(2) | -111.71(12) |
| C(16)-C(17)-Ru(2)-C(19) | -80.13(13) |
| C(18)-C(17)-Ru(2)-C(19) | 38.28(12) |
| C(16)-C(17)-Ru(2)-C(15) | -37.75(12) |
| C(18)-C(17)-Ru(2)-C(15) | 80.65(13) |
| C(16)-C(17)-Ru(2)-C(18) | -118.40(18) |
| C(18)-C(17)-Ru(2)-C(16) | 118.40(18) |
| C(17)-C(16)-Ru(2)-C(21) | -149.61(13) |
| C(15)-C(16)-Ru(2)-C(21) | 92.97(14) |
| C(17)-C(16)-Ru(2)-C(20) | 98.5(2) |
| C(15)-C(16)-Ru(2)-C(20) | -19.0(3) |
| C(17)-C(16)-Ru(2)-N(2) | -56.62(13) |
| C(15)-C(16)-Ru(2)-N(2) | -174.03(11) |
| C(17)-C(16)-Ru(2)-C(19) | 79.61(13) |
| C(15)-C(16)-Ru(2)-C(19) | -37.81(12) |
| C(17)-C(16)-Ru(2)-C(15) | 117.42(18) |
| C(17)-C(16)-Ru(2)-C(18) | 36.87(12) |
| C(15)-C(16)-Ru(2)-C(18) | -80.54(13) |
| C(15)-C(16)-Ru(2)-C(17) | -117.42(18) |

**Cyclopentadienyl ruthenium(II) allylamine complex - $[\eta^5$-$C_5H_5Ru(CO)_2NH_2CH_2CHCH_2]BF_4$.**



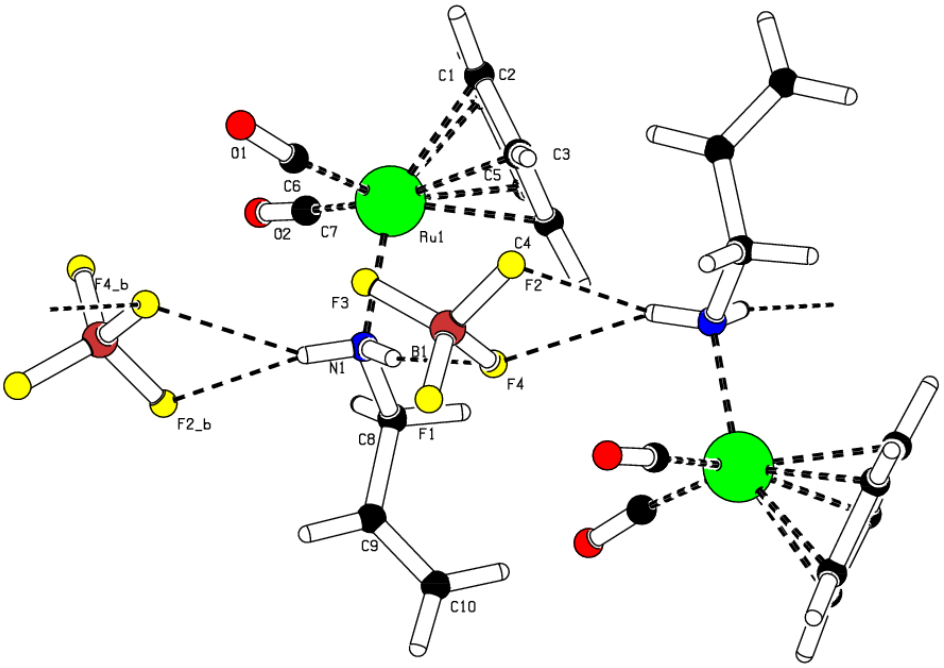



**Table B66:** Crystal data and structure refinement for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2CHCH_2]BF_4$.

| | | |
|---|---|---|
| Identification code | shelx | |
| Empirical formula | C10 H12 B F4 N O2 Ru | |
| Formula weight | 366.09 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P 21/n | |
| Unit cell dimensions | a = 8.7303(3) Å | α= 90°. |
| | b = 9.7841(3) Å | β= 91.5250(10)°. |
| | c = 15.4342(5) Å | γ = 90°. |
| Volume | 1317.89(7) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.845 $Mg/m^3$ | |
| Absorption coefficient | 1.232 $mm^{-1}$ | |
| F(000) | 720 | |
| Crystal size | 0.360 x 0.250 x 0.240 $mm^3$ | |
| Theta range for data collection | 2.465 to 28.307°. | |
| Index ranges | -11<=h<=11, -12<=k<=13, -20<=l<=20 | |
| Reflections collected | 25223 | |
| Independent reflections | 3282 [R(int) = 0.0242] | |
| Completeness to theta = 25.242° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.744 and 0.698 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3282 / 0 / 180 | |
| Goodness-of-fit on $F^2$ | 1.050 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0195, wR2 = 0.0455 | |
| R indices (all data) | R1 = 0.0223, wR2 = 0.0475 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.850 and -0.661 $e.Å^{-3}$ | |

**Table B67:** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2CHCH_2]BF_4$. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 5687(2) | 1776(2) | 9857(1) | 30(1) |
| C(2) | 4095(2) | 1708(2) | 9674(2) | 36(1) |
| C(3) | 3874(2) | 1086(2) | 8846(2) | 38(1) |
| C(4) | 5329(2) | 779(2) | 8521(1) | 30(1) |
| C(5) | 6457(2) | 1212(2) | 9140(1) | 27(1) |
| C(6) | 6508(2) | 4444(2) | 9099(1) | 26(1) |
| C(7) | 3445(2) | 4264(2) | 8624(1) | 28(1) |
| C(8) | 4470(2) | 3022(2) | 6734(1) | 28(1) |
| C(9) | 4895(2) | 3330(2) | 5824(1) | 29(1) |
| C(10) | 4972(2) | 2400(3) | 5211(1) | 37(1) |
| N(1) | 5666(2) | 3438(2) | 7385(1) | 20(1) |
| O(1) | 7340(2) | 5205(2) | 9402(1) | 42(1) |
| O(2) | 2381(2) | 4936(2) | 8605(1) | 44(1) |
| B(1) | -332(2) | 2228(2) | 7552(1) | 26(1) |
| F(1) | 655(2) | 2500(2) | 6908(1) | 76(1) |
| F(2) | 339(2) | 1316(1) | 8132(1) | 45(1) |
| F(3) | -770(1) | 3412(1) | 7972(1) | 37(1) |
| F(4) | -1648(2) | 1574(2) | 7229(1) | 61(1) |
| Ru(1) | 5139(1) | 3053(1) | 8709(1) | 18(1) |

**Table B68:** Bond lengths [Å] and angles [°] for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2CHCH_2]BF_4$.

| | |
|---|---|
| C(1)-C(2) | 1.412(3) |
| C(1)-C(5) | 1.421(3) |
| C(1)-Ru(1) | 2.2092(18) |
| C(1)-H(1) | 1.0000 |
| C(2)-C(3) | 1.425(3) |
| C(2)-Ru(1) | 2.2029(19) |
| C(2)-H(2) | 1.0000 |
| C(3)-C(4) | 1.410(3) |
| C(3)-Ru(1) | 2.2320(19) |
| C(3)-H(3) | 1.0000 |
| C(4)-C(5) | 1.419(3) |
| C(4)-Ru(1) | 2.2509(18) |
| C(4)-H(4) | 1.0000 |
| C(5)-Ru(1) | 2.2300(17) |
| C(5)-H(5) | 1.0000 |
| C(6)-O(1) | 1.132(2) |
| C(6)-Ru(1) | 1.8989(19) |
| C(7)-O(2) | 1.138(2) |
| C(7)-Ru(1) | 1.8958(18) |
| C(8)-N(1) | 1.487(2) |
| C(8)-C(9) | 1.492(3) |
| C(8)-H(8A) | 0.9900 |
| C(8)-H(8B) | 0.9900 |
| C(9)-C(10) | 1.316(3) |
| C(9)-H(9) | 0.9500 |
| C(10)-H(10A) | 0.9500 |
| C(10)-H(10B) | 0.9500 |
| N(1)-Ru(1) | 2.1399(14) |
| N(1)-H(1A) | 0.85(2) |
| N(1)-H(1B) | 0.85(2) |
| B(1)-F(1) | 1.359(2) |
| B(1)-F(2) | 1.383(2) |
| B(1)-F(3) | 1.386(2) |
| B(1)-F(4) | 1.395(2) |
| | |
| C(2)-C(1)-C(5) | 108.06(18) |

| | |
|---|---|
| C(2)-C(1)-Ru(1) | 71.09(11) |
| C(5)-C(1)-Ru(1) | 72.12(10) |
| C(2)-C(1)-H(1) | 125.9 |
| C(5)-C(1)-H(1) | 125.9 |
| Ru(1)-C(1)-H(1) | 125.9 |
| C(1)-C(2)-C(3) | 107.96(18) |
| C(1)-C(2)-Ru(1) | 71.57(11) |
| C(3)-C(2)-Ru(1) | 72.36(11) |
| C(1)-C(2)-H(2) | 125.9 |
| C(3)-C(2)-H(2) | 125.9 |
| Ru(1)-C(2)-H(2) | 125.9 |
| C(4)-C(3)-C(2) | 107.92(18) |
| C(4)-C(3)-Ru(1) | 72.40(11) |
| C(2)-C(3)-Ru(1) | 70.15(11) |
| C(4)-C(3)-H(3) | 126.0 |
| C(2)-C(3)-H(3) | 126.0 |
| Ru(1)-C(3)-H(3) | 126.0 |
| C(3)-C(4)-C(5) | 108.26(18) |
| C(3)-C(4)-Ru(1) | 70.93(11) |
| C(5)-C(4)-Ru(1) | 70.74(10) |
| C(3)-C(4)-H(4) | 125.8 |
| C(5)-C(4)-H(4) | 125.8 |
| Ru(1)-C(4)-H(4) | 125.8 |
| C(4)-C(5)-C(1) | 107.79(17) |
| C(4)-C(5)-Ru(1) | 72.35(10) |
| C(1)-C(5)-Ru(1) | 70.53(10) |
| C(4)-C(5)-H(5) | 126.0 |
| C(1)-C(5)-H(5) | 126.0 |
| Ru(1)-C(5)-H(5) | 126.0 |
| O(1)-C(6)-Ru(1) | 173.55(15) |
| O(2)-C(7)-Ru(1) | 175.78(17) |
| N(1)-C(8)-C(9) | 113.12(15) |
| N(1)-C(8)-H(8A) | 109.0 |
| C(9)-C(8)-H(8A) | 109.0 |
| N(1)-C(8)-H(8B) | 109.0 |
| C(9)-C(8)-H(8B) | 109.0 |
| H(8A)-C(8)-H(8B) | 107.8 |
| C(10)-C(9)-C(8) | 123.8(2) |

| | |
|---|---|
| C(10)-C(9)-H(9) | 118.1 |
| C(8)-C(9)-H(9) | 118.1 |
| C(9)-C(10)-H(10A) | 120.0 |
| C(9)-C(10)-H(10B) | 120.0 |
| H(10A)-C(10)-H(10B) | 120.0 |
| C(8)-N(1)-Ru(1) | 115.62(11) |
| C(8)-N(1)-H(1A) | 108.9(15) |
| Ru(1)-N(1)-H(1A) | 107.8(15) |
| C(8)-N(1)-H(1B) | 106.4(14) |
| Ru(1)-N(1)-H(1B) | 110.1(14) |
| H(1A)-N(1)-H(1B) | 108(2) |
| F(1)-B(1)-F(2) | 109.53(17) |
| F(1)-B(1)-F(3) | 111.48(18) |
| F(2)-B(1)-F(3) | 110.71(16) |
| F(1)-B(1)-F(4) | 111.16(19) |
| F(2)-B(1)-F(4) | 105.42(17) |
| F(3)-B(1)-F(4) | 108.37(16) |
| C(7)-Ru(1)-C(6) | 93.30(8) |
| C(7)-Ru(1)-N(1) | 90.63(7) |
| C(6)-Ru(1)-N(1) | 91.56(7) |
| C(7)-Ru(1)-C(2) | 94.84(8) |
| C(6)-Ru(1)-C(2) | 118.82(8) |
| N(1)-Ru(1)-C(2) | 148.65(8) |
| C(7)-Ru(1)-C(1) | 124.11(8) |
| C(6)-Ru(1)-C(1) | 91.72(7) |
| N(1)-Ru(1)-C(1) | 144.81(7) |
| C(2)-Ru(1)-C(1) | 37.34(8) |
| C(7)-Ru(1)-C(5) | 157.03(7) |
| C(6)-Ru(1)-C(5) | 99.73(7) |
| N(1)-Ru(1)-C(5) | 107.71(6) |
| C(2)-Ru(1)-C(5) | 62.31(7) |
| C(1)-Ru(1)-C(5) | 37.35(7) |
| C(7)-Ru(1)-C(3) | 99.10(8) |
| C(6)-Ru(1)-C(3) | 153.80(8) |
| N(1)-Ru(1)-C(3) | 111.17(7) |
| C(2)-Ru(1)-C(3) | 37.48(8) |
| C(1)-Ru(1)-C(3) | 62.23(8) |
| C(5)-Ru(1)-C(3) | 61.83(7) |

| | |
|---|---|
| C(7)-Ru(1)-C(4) | 131.95(8) |
| C(6)-Ru(1)-C(4) | 134.55(8) |
| N(1)-Ru(1)-C(4) | 91.83(7) |
| C(2)-Ru(1)-C(4) | 61.96(8) |
| C(1)-Ru(1)-C(4) | 61.92(7) |
| C(5)-Ru(1)-C(4) | 36.91(7) |
| C(3)-Ru(1)-C(4) | 36.67(8) |

**Table B69:** Anisotropic displacement parameters ($Å^2$ x $10^3$)for [$\eta^5$-$C_5H_5Ru(CO)_2NH_2CH_2CHCH_2]BF_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 43(1) | 21(1) | 26(1) | 9(1) | 2(1) | 2(1) |
| C(2) | 36(1) | 25(1) | 48(1) | 15(1) | 18(1) | 3(1) |
| C(3) | 31(1) | 23(1) | 59(1) | 13(1) | -8(1) | -7(1) |
| C(4) | 45(1) | 12(1) | 34(1) | 1(1) | 0(1) | 1(1) |
| C(5) | 27(1) | 20(1) | 34(1) | 8(1) | 1(1) | 6(1) |
| C(6) | 38(1) | 22(1) | 19(1) | 4(1) | -2(1) | 0(1) |
| C(7) | 32(1) | 26(1) | 25(1) | 4(1) | 6(1) | 6(1) |
| C(8) | 26(1) | 34(1) | 24(1) | -1(1) | -6(1) | -5(1) |
| C(9) | 30(1) | 33(1) | 24(1) | 3(1) | -6(1) | 0(1) |
| C(10) | 31(1) | 52(1) | 27(1) | -6(1) | -6(1) | 5(1) |
| N(1) | 19(1) | 19(1) | 21(1) | -1(1) | 0(1) | -1(1) |
| O(1) | 61(1) | 33(1) | 31(1) | -1(1) | -14(1) | -17(1) |
| O(2) | 41(1) | 45(1) | 47(1) | 9(1) | 9(1) | 24(1) |
| B(1) | 24(1) | 28(1) | 25(1) | 2(1) | 1(1) | 5(1) |
| F(1) | 83(1) | 71(1) | 77(1) | 33(1) | 58(1) | 28(1) |
| F(2) | 59(1) | 32(1) | 45(1) | 9(1) | -12(1) | 9(1) |
| F(3) | 43(1) | 24(1) | 43(1) | -2(1) | 5(1) | 1(1) |
| F(4) | 33(1) | 72(1) | 78(1) | -48(1) | -20(1) | 17(1) |
| Ru(1) | 19(1) | 15(1) | 20(1) | 2(1) | 1(1) | 1(1) |

**Table B70:** Torsion angles [°] for $[\eta^5\text{-}C_5H_5Ru(CO)_2NH_2CH_2CHCH_2]BF_4$.

| | |
|---|---|
| C(5)-C(1)-C(2)-C(3) | 0.6(2) |
| Ru(1)-C(1)-C(2)-C(3) | 63.66(13) |
| C(5)-C(1)-C(2)-Ru(1) | -63.06(12) |
| C(1)-C(2)-C(3)-C(4) | -0.2(2) |
| Ru(1)-C(2)-C(3)-C(4) | 62.96(13) |
| C(1)-C(2)-C(3)-Ru(1) | -63.15(13) |
| C(2)-C(3)-C(4)-C(5) | -0.3(2) |
| Ru(1)-C(3)-C(4)-C(5) | 61.22(13) |
| C(2)-C(3)-C(4)-Ru(1) | -61.51(13) |
| C(3)-C(4)-C(5)-C(1) | 0.7(2) |
| Ru(1)-C(4)-C(5)-C(1) | 62.00(12) |
| C(3)-C(4)-C(5)-Ru(1) | -61.34(13) |
| C(2)-C(1)-C(5)-C(4) | -0.8(2) |
| Ru(1)-C(1)-C(5)-C(4) | -63.18(12) |
| C(2)-C(1)-C(5)-Ru(1) | 62.40(13) |
| N(1)-C(8)-C(9)-C(10) | 122.3(2) |
| C(9)-C(8)-N(1)-Ru(1) | 179.32(13) |

# APPENDIX C

## Gas chromatography-based calculation of % conversion and % yield

1. Calculate the Response factor (RF) for the substrate, all possible products and the internal standard (IS).

   $$Response\ Factor\ (RF) = {Peak\ area}/{No.of\ moles}$$

2. Calculate the relative response factor (RRF) for the substrate and each product

   $$RRF = {RF}/{RF\ (IS)}$$

   NB: RRF for the internal standard = 1

3. Calculate the RF for the internal standard for each reaction and use it to, calculate the moles of substrate left at the end of each reaction and the moles of each product formed
   a) Calculate the response factor for each product and substrate at the end of each reaction

      $$RF = RRF\ \times RF\ (IS)$$

   b) Calculate moles of each product formed and substrate left at the end of the reaction

      i. $$Moles = {peak\ area}/{RF}$$

      ii. $$\%\ yield = \left({No.of\ moles\ found}/{Expected\ no\ of\ moles}\right) \times 100$$

      iii. $$\%\ Conversion = \left({(inial\ no.of\ moles - No.of\ moles\ left)}/{Initial\ no.of\ moles}\right) \times 100$$

# ANTIMICROBIAL SUSCEPTIBILITY TEST RESULTS – SAMPLE PHOTOS

Sample photos illustrating antimicrobial activity of 1,6-diaminohexane ruthenium and iron complexes against the gram positive bacteria *M. smegmatis* $mc^2155$

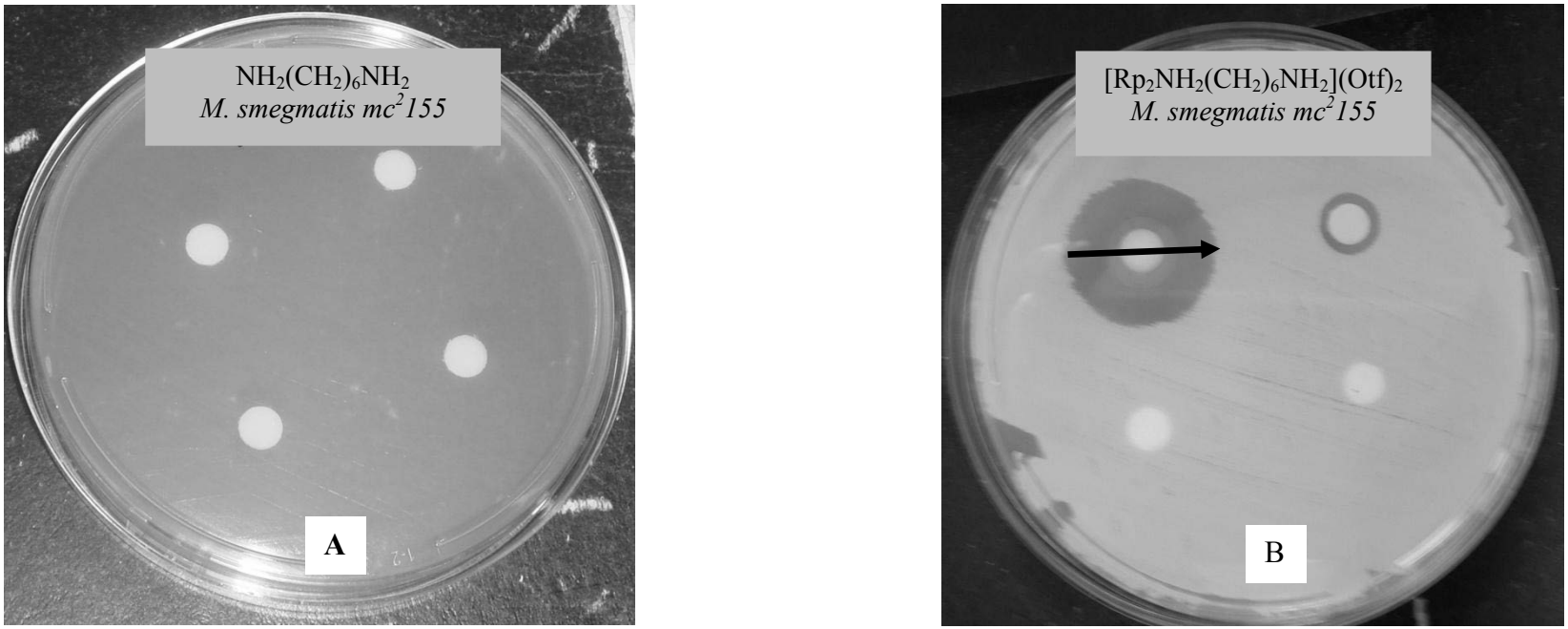



**Figure 1D:** Zone inhibition by (A) 1,6-diaminohexane and $[Rp_2NH_2(CH_2)_6NH_2](SO_3CF_3)_2$ (B) against the bacteria *M. smegmatis mc²155* Bottom discs in each plate contain the free ligand, 1,6-diaminohexane

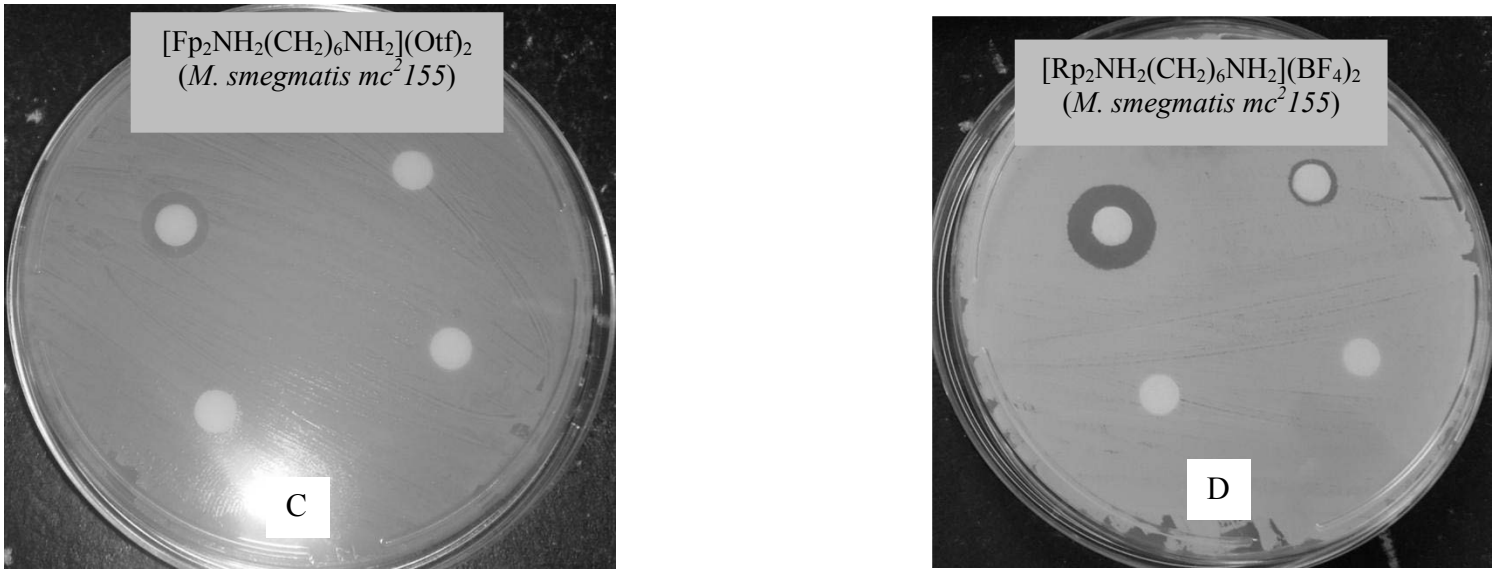



**Figure 2D:** Zone inhibition by $[Fp_2NH_2(CH_2)_6NH_2](SO_3CF_3)_2$ (top) (C) and $[Rp_2NH_2(CH_2)_6NH_2](BF_{43})_2$ (top) (D) against the bacteria *M. smegmatis mc²155*
Bottom discs in each plate contain the free ligand, 1,6-diaminohexane

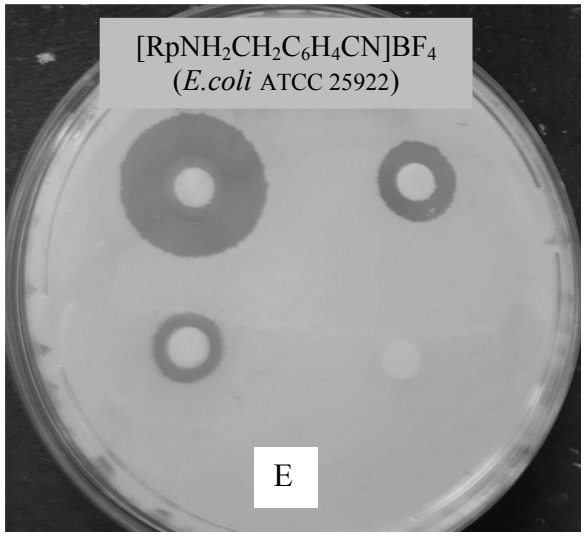



**Figure 2D:** Zone inhibition by $[RpNH_2CH_2C_6H_4CN]BF_4$ (top) and the free ligand 4-aminomethylbenzonitrile (bottom) the bacteria *E.coli* ATCC 25922